THE PREPARATION, CHARACTERIZATION AND CATALYTIC ACTIVITY OF A NEW SOLID ACID CATALYST SYSTEM

By

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To my parents

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I would like to express my gratitude to Professor Russell S. Drago for his support and encouragement over the past four years. Doc made my years in graduate school very enjoyable both in the lab and on the tennis court. I would also like to thank Ruth Drago for making Florida seem like a home.

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The preparation and use of solid strong acid catalysts and superacids are active areas of research. Solid acids and superacids are reported to exhibit extremely high catalytic activities for reactions such as isomerization, cracking, hydrocracking, dehydration, alkylation, acylation, conversion of methanol to gasoline, and so forth. Recent research in this area has focused on the preparation of stronger solid acids and their characterization. Advantages of solid acid catalysts over liquid acid catalysts include ease of separation from reaction mixture and high selectivity or specific activity.

A series of novel solid strong acids has been prepared by treatment of inorganic oxides by Lewis acids. The method of creating or enhancing the number of tetrahedral aluminum centers on inorganic oxides has led to a series of novel solid acid catalysts which displays an increased acidity over the supports alone.

Investigations of acid sites by the infrared spectroscopy of adsorbed pyridine, calorimetric titrations and solid-state nuclear magnetic resonance on a series of new solid acid catalysts will be discussed. This new solid acid catalyst system exhibits high catalytic activity and selectivity for cracking reactions under relatively mild conditions. In addition to the reactions of hydrocarbons, the reactions of various polychlorinated molecules have been studied.

CHAPTER I
INTRODUCTION

Since the introduction of amorphous silica-alumina solid acids over 40 years ago, catalytic cracking has become one of the world's most important processes for the refining of petroleum.[1] The popularity of the catalytic cracking process results from its flexibility in treating a variety of feedstocks used in refinery processes.[1-3] Temperatures of 450-550°C and pressures of 1-2 atm are typical reaction conditions.[2] Amorphous silica-aluminas and zeolites are the most common catalysts used and recent trends in catalytic cracking research are aimed at enhancing the acidity of these catalysts.[4]

The preparation and use of strong solid acids and superacids as catalysts are active areas of research.[4,5] These materials exhibit extremely high catalytic activity for reactions such as isomerization, cracking, hydrocracking, dehydration, alkylation, acylation, conversion of methanol to gasoline, and so forth.[4,5] Advantages of solid acid catalysts over liquid acid catalysts include ease of separation from reaction mixture and high selectivity or specific activity.[4]

In view of the higher activity of tetrahedral aluminum Lewis acids than octahedral Lewis acids, we are interested in preparing solids containing stable tetrahedral aluminum sites. As a result

of this research a new solid, strong acid catalyst system is reported which exhibits high catalytic activity and selectivity for catalytic cracking reactions under relatively mild conditions. In the following chapters the synthesis, characterization, and catalytic activity for these new solid acid catalyst systems are reported.

The synthesis, characterization, and catalytic activity of these catalysts for the catalytic cracking of hydrocarbons is discussed in Chapter II. The synthesis and catalytic activity of various solid acid catalysts doped with metals is discussed in Chapter III. In addition to cracking, the dehydrochlorination and hydrodechlorination of various polychlorinated hydrocarbons is reported.

CHAPTER II
REACTION OF HYDROCARBONS

2.1 BACKGROUND

Since the introduction of acid-treated clays and amorphous silica-alumina solid acids as cracking catalysts in the late 1930s, catalytic cracking has become the most important process for the refining of crude petroleum in the world.[1-3] In 1985 the petroleum industry bought 370 million lbs of catalytic cracking catalysts at a cost of 250 million dollars. The projected use of catalytic cracking catalysts in 1990 is expected to increase to 405 million lbs which is worth 275 million dollars.[6] Because of the large volumes of solid acid cracking catalysts used and the importance of the petroleum refining process, a large amount of research has been conducted in the area of solid acid and superacid catalysis.[1-6]

Currently, the preparation and use of strong acid catalysts and superacids are active areas of research. These materials exhibit extremely high catalytic activity for reactions such as isomerization, cracking, hydrocracking, dehydration, alkylation, acylation, conversion of methanol to gasoline, and so forth.[5] Because of the reported advantages of solid acid catalysts[4],

recent research has focused on the preparation and characterization[2,4,5] of stronger solid acids.

Many attempts have been made to use metal halides as homogeneous acid catalysts and one of the most frequently studied inorganic Lewis acid metal halides is aluminum chloride. Aluminum chloride was even tested commercially but was abandoned because of technical difficulties such as corrosion, separation of phases, difficulty in the recovery of the catalyst and the formation of high molecular weight hydrocarbons.[2,3] As a result recent research has focused on the anchoring of homogeneous acid catalysts onto inorganic oxides for use as solid acid catalysts.[2-7]

Many patents have been issued for the treatment of inorganic oxides with aluminum chloride.[8-15] The most common method of treating hydroxylated inorganic oxides with aluminum chloride is by vapor deposition.[4,8-14] The vapor deposition is conducted by passing the vapors of aluminum chloride through the inorganic oxide using a carrier gas such as helium[7,9,10,12,14] or sublimation of the aluminum chloride from a mixture of the inorganic oxide and aluminum chloride.[11,14] An alternative to the vapor deposition of the aluminum chloride is the reaction of aluminum chloride and the inorganic oxide in a chlorinated or hydrocarbon solvent.[8]

Past attempts[8] conducted on this reaction have employed solvents other than carbon tetrachloride (CCl_4). It has been determined that chloroform ($CHCl_3$), methylene chloride (CH_2Cl_2), ethylene dichloride ($ClCH_2CH_2Cl$) and saturated hydrocarbons (to name

a few) do not produce a solid acid catalyst with the properties described for the reaction employing CCl_4.[15]

In each of these cases (except CCl_4) aluminum chloride is evolved from the catalyst surface with time and only short term activity results.[4,8-14] This is in contrast to what has been found for the inorganic oxides treated with aluminum chloride in CCl_4 by the procedure reported here.[15]

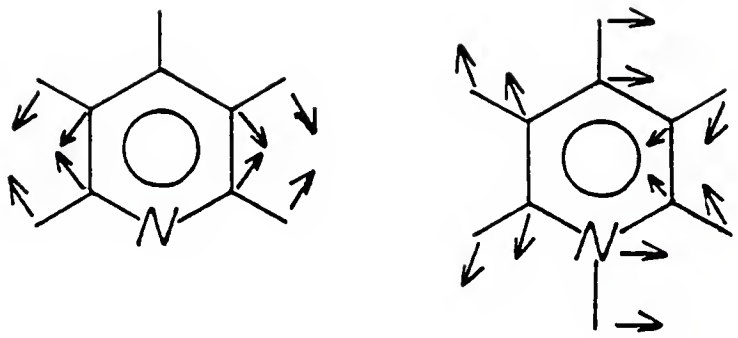
Since it is known that the catalytic properties of these amorphous silica-alumina catalysts arises from the acidity[1-3] many methods have been developed to characterize the acidity of these catalysts.[1-3,16-25] Using changes in the infrared spectra of adsorbed basic molecules on solid acids to determine the nature and strength of the acid sites present has been practiced extensively.[16-27] Some of the early work in this area was performed by E. Parry in the early 1960's.[16] In this method, pyridine is allowed to interact with the solid acid surface and changes in the infrared adsorptions in the 1400 cm^{-1} to 1700 cm^{-1} region for pyridine are measured. When pyridine is adsorbed on an acid site which has protonic character, infrared adsorptions indicative of pyridinium ion are observed at 1485-1500 cm^{-1}, 1540 cm^{-1}, ~1620 cm-1 and ~1640 cm^{-1}.[16-18] The infrared band at 1540 cm^{-1} involves the A_1 bending mode for pyridinium ion including the C-N-C as well as the N^+-H bending motion.[21-24] Since the 1540 cm^{-1} band is not present for pyridine bound to other Lewis acid sites, it is used along with the other bands to characterize protonic (Bronsted) sites.[16] When pyridine is adsorbed on a non-protonic

(Lewis) acid the infrared adsorptions indicative of coordinately bound pyridine are observed at 1447-1460 cm^{-1}, 1488-1503 cm^{-1}, ~1580 cm^{-1} and 1600-1635 cm^{-1}.[21-24] The infrared band in the 1447-1460 cm^{-1} region involves the A_1 bending mode, C-N-C, and is used to characterize coordinatively bonded pyridine, Figure 2-1. As the Lewis acid strength of the acid site increases the band is reported[16] to shift to higher frequencies.

Extensive research has been conducted on the vibrational spectra of benzene and pyridine. The assignments of the frequencies have been reported in the literature.[27,28]

The use of solid-state Magic-Angle-Spinning (MAS) NMR spectroscopy as a spectroscopic tool to characterize heterogeneous catalysts has bee widely documented.[29-33] A large amount of work has focused on the ^{27}Al and ^{29}Si solid-state MAS NMR spectra of silica-aluminas, aluminosilicates and zeolites.[29] By the use of ^{27}Al and ^{29}Si MAS NMR spectroscopy it has been shown that 4-coordinate and 6-coordinate aluminum exhibit different chemical shifts with large enough separation that they can be distinguished even if they coexist in the same sample.[29,30]

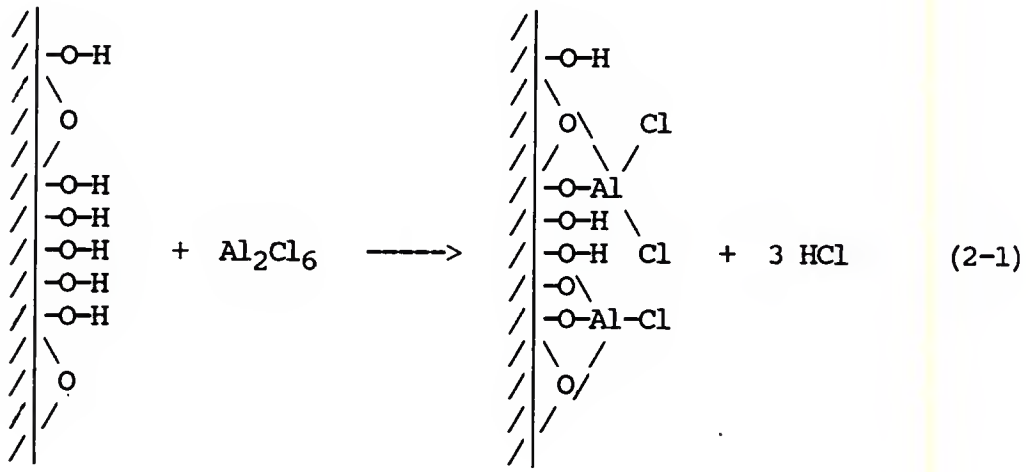
It has been generally accepted that 4-coordinate aluminum, such as that in zeolites, has a chemical shift in the 50-65 ppm region relative to an $Al^{3+}(aq)$ standard.[30] A chemical shift of 58 ppm relative to a $Al^{3+}(aq)$ standard has been observed for zeolitic aluminum centers generated by the reaction of aluminum chloride with ZSM-5 zeolite by vapor phase deposition.[33] The chemical shift for



8a 19b

Figure 2-1. The A_1 Bending Modes for Pyridine.

framework Al in gamma-Al_2O_3 has been reported to occur at 50 ppm relative to an Al^{3+}(aq) standard.[33] The ^{27}Al NMR of an aqueous $Al(NO_3)_3$ solution is the reference for all our ^{27}Al MAS NMR work. Since the reference is a 6-coordinate octahedral complex, a peak between 50 and 100 ppm down field from Al^{3+}(aq) would be expected if the aluminum chloride has retained its tetrahedral geometry. The chemical shift for aluminum chlorohydrate is reported[31] to be 62.8 ppm versus Al^{3+}(aq) which would be near the peak expected for a surface-bound chloroaluminum species formed by the reaction of aluminum chloride and a hydroxylated inorganic oxide,[8-14] Equation 2-1.



The chemical shift for Al_2Cl_6 in solution has been reported to occur at 91-105 ppm and the chemical shift for $AlCl_4^-$ has been reported to occur at 100-110 ppm depending on the solvent.[32]

When aluminum chloride reacts with an inorganic oxide (such as silica gel), tetrahedral aluminum centers are formed on the oxide surface.[8-14,34] These tetrahedral aluminum centers should have properties similar to free aluminum chloride and hence should have

similar catalytic activity. It can be determined using solid-state MAS NMR if the aluminum chloride that is reacted with an inorganic oxide has retained its tetrahedral conformation. Furthermore, the ^{27}Al chemical shifts for Al_2Cl_6 and $AlCl_4^-$ are much higher than for the oxychloroaluminum species. It should be easy to distinguish the Al_2Cl_6 and $AlCl_4^-$ species from surface bound oxyaluminum species by ^{27}Al MAS NMR.

The following chapter is concerned with the preparation of aluminum chloride treated inorganic oxides by a previously unreported method.[15] The characterization by Infrared and NMR spectroscopy as well as an in depth study of the catalytic activity of the aluminum chloride treated supports is discussed to support the claim that a new solid, strong acid has been discovered with this new method of preparation.

2.2 EXPERIMENTAL

Reagents

All metal halides were used as purchased unless otherwise stated. The palladium (II) chloride ($PdCl_2$) and rhodium (II) chloride ($RhCl_3$) were purchased from Aldrich Chemical Company (Aldrich). Aluminum chloride (Al_2Cl_6) with a purity of 99.997% was purchased from Alfa Products. The iron (III) chloride ($FeCl_3$) and antimony (V) chloride ($SbCl_5$) were purchased from AESAR. All solvents were purchased from Fisher Scientific Co. (Fisher) except tetrachloroethylene which was purchased from Eastman Kodak Co.

(Kodak), n-dodecane and n-hexadecane which were purchased from Alfa Products. Carbon tetrachloride, chloroform and methylene chloride were dried over phosphorous (V) oxide (Fisher). Benzene was dried by distillation over calcium hydride. Cyclohexane and chloroform (containing ethanol as a stabilizer) were purified by passage through an activated alumina column. Tetrachloroethane, n-pentane, n-hexane, n-heptane, n-dodecane, n-hexadecane and cumene were used as purchased. Gold label (99+%) pyridine was purchased from Aldrich and was used without further purification. All solvents were stored over 4A molecular sieves (Davison Chemical). The gaseous reactants methane, dimethyl ether, propylene, propane, isobutane, technical grade hydrogen chloride (99.0%), and C.P. Grade carbon monoxide (99.5%) were purchased from Matheson. Hydrogen, helium, argon and nitrogen were supplies by Airco and Liquid Air. The semiconductor-grade hydrogen chloride (99.995%) was purchased from Air Products. The supports used for the preparation of the catalysts are silicon dioxide (SiO_2), alumina (Al_2O_3), high-silica zeolite (silicalite), Y-zeolite (LZ-Y82), boron oxide (B_2O_3), titanium dioxide (TiO_2) and magnesium oxide (MgO). All support materials were used as purchased unless otherwise stated. For the silicon dioxide supports the primary material was Davison Grade #62 silicon dioxide (donated by W.R. Grace Co.) with a surface area of 340 m^2/gram, pore volume of 1.1 cm^2/gram and a mess size of 60-200.[35] The three types of silicon dioxide support materials used for surface area dependence studies were purchased from AESAR. All three supports are 60-325 mesh size with surface areas of 215 m^2/gram, 420 m^2/gram, 690

m^2/gram and pore volumes of 1.0 cm^3/gram, 0.8 cm^3/gram and 0.4 cm^3/gram, respectively. The alumina support, acid Brockman Activity I (80-120 mesh), had a surface area of 180 m^2/gram.[35] A high-silica zeolite which was donated by Union Carbide had a surface area of 400 m^2/gram and a pore volume of 0.19 cm^3/gram. The Y-zeolite was a Linde LZ-Y82 molecular sieve purchased from Alfa Products and is used commercially as a fluid catalytic cracking (FCC) catalyst. The boron oxide was purchased from AESAR and had a mesh size of 60. Bayer AG donated the hydroxylated titanium dioxide (surface area 200 m^2/gram) and the magnesium oxide was purchased from Fisher. 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) which is a diamagnetic spin trapping agent was purchased from Aldrich. Other reactants used for cracking reactions were activated carbon (Curtin, MCB) and resid (FHC-353 donated by Amoco) which is a mixture of high molecular weight hydrocarbons obtained from the distillation of heavy crude oil. Monomers used for polymerization reactions were isobutane (Matheson), styrene (Fisher), methyl methacrylate (Fisher), methacrylate (Fisher), vinyl acetate (Aldrich), ethyl vinyl ether (Aldrich) and epichlorohydrin (Kodak). Purification of monomers were conducted by literature methods.

Instrumentation

All air and water sensitive manipulations were performed in a Vacuum Atmosphere Company model HE-43-2 inert atmosphere box or in an Aldrich inert atmosphere glove bag. All syntheses were conducted under a nitrogen or argon atmosphere and one atmosphere pressure.

Routine GC analysis for hydrocarbon products were performed on a model 940 FID Varian gas chromatograph equipped with a Hewlett-Packard 3390A integrator and a 1/8 inch by 8 foot stainless steel Porapak Q (100-120 mesh) column or a 1/8 inch by 6 foot stainless steel Hayesep Q (80-100 mesh) column. Routine GC analysis for chlorinated hydrocarbons were performed on a model 3700 TCD Varian gas chromatograph equipped with a Hewlett-Packard 3390A integrator and a 1/8 inch by 8 foot Porapak Q (100-120 mesh) column. The GC FTIR was performed on a Nicolet 5DXB FTIR spectrometer equipped with a Nicolet GC interface and a Hewlett-Packard 5890A gas chromatograph using a 1.5 micron thick DB 130m fused silica capillary column that was 30 meters in length. EPR spectra were obtained from a Bruker ER200D-SRC spectrometer equipped with a variable temperature unit, ER 022 signal channel controller, ER 001 time base controller, ER 031M field controller, ER 082 power supply and ER 040XR microwave bridge. GC mass spectrometry was performed by Dr. Roy King of the Microanalytical Laboratory, University of Florida, Gainesville, Florida. Gas samples were analyzed on a AEI MS 30 mass spectrometer with a KOITOS DS55 data station. The system was connected to a PYE Unicam 104 gas chromatograph equipped with a 1/4 inch by 5 foot glass Porapak Q (100-120 mesh) column. Solid-state magic angle spinning (MAS) nuclear magnetic resonance spectra were collected by Dr. W. S. Brey of the University of Florida, Gainesville, Florida, on a Nicolet NT-300 300 mHz wide-bore superconducting FT-NMR spectrometer. Infrared spectra were obtained as mulls on a nicolet 5DXB FT-IR spectrometer using KBr plates. All solid-liquid phase

cracking reactions and polymerizations were carried out in 250 mL or 500 mL Parr pressure bottles equipped with a brass or stainless steel swagelok pressure heads and neoprene stoppers.[36]

Fixed Bed Flow Reactor

A fixed-bed flow reactor was constructed as described by Keith Weiss and reported in his Ph.D. Dissertation.[35] The reactor was modified by placing a hydrocarbon bubbler after the reactant gas bubblers and before the catalyst zone to allow the addition of a hydrocarbon substrate. The modified reactor allowed the experimenter to saturate the reactant and carrier gases with any liquid hydrocarbon substrate that has an appreciable vapor pressure. The flow rates of the individual gases were controlled by teflon needle valves. Hydrogen and helium were passed through mineral oil bubblers whereas the HCl was bubbled through sulfuric acid. The gases were allowed to mix and pass through bubbler which contained a hydrocarbon/carbon tetrachloride mixture. This gas mixture was then allowed to flow through a catalyst which was supported on a glass frit. The catalyst zone was heated by a Thermolyne Briskheat flexible electric heat tape controlled by an Omega Engineering, Inc. digital temperature controller, model CN 310 equipped with a J-Type thermocouple. Pregas and post gas samples for GC analysis could be obtained through sample ports before and after the catalyst zone. Overall flow rates for the reactor system were monitored by a calibrated bubble flow meter. The entire reactor was constructed of glass and was custom built by glass blowers Rudy Schroschein and

Dick Moshier at the glass shop, University of Florida, Gainesville, Florida.

This reactor was further modified using a syringe pump to deliver liquid reactants to the catalyst in place of a hydrocarbon or hydrocarbon/carbon tetrachloride bubbler.[37] A preheater zone was added to the system to ensure proper mixing and heating of all reactants before they were contacted with the catalyst. Typically only one gas was used as a carrier gas and/or reactant gas. The gas flow rate was regulated by a calibrated rotoflow meter purchased from Gilmont Instruments, Inc.

Preparation of a Silica Gel Catalyst Doped with Aluminum Chloride Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 10.20 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs) and 150 mL of carbon tetrachloride (dried over 4 A sieves). After purging the system with nitrogen (N_2), 5.10 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 1-5 days in the absence of light.

After approximately 1 hour the mixture developed a purple color. This color continued to increase in intensity until the mixture was black in appearance (~8 hours).

After 5 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was burgundy in color and was utilized as the

catalyst material for the cracking experiments described later in this chapter. The catalyst was water-sensitive and turned white on exposure to moisture.

The catalyst gave an EPR signal indicative of a free-radical with a g value of 2.012, Figure 2-2. If after the purple color first appears, to approximately 1 days, the mixture is filtered, the catalyst obtained will show an EPR signal which is very broad and has a g value of 2.06, Figure 2-3.

Preparation of an Alumina Catalyst Doped with Aluminum Chloride Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 15.0 grams of alumina (dried at 150°C) and 175 mL of carbon tetrachloride (dried over 4 A sieves). After purging the system with nitrogen (N_2), 7.5 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 2 days in the absence of light.

After approximately 1 hour the mixture developed a purple color. This color continued to increase in intensity until the mixture was black in appearance.

After 2 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate had a slight red color and the resulting solid product obtained was purple in appearance.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.012.

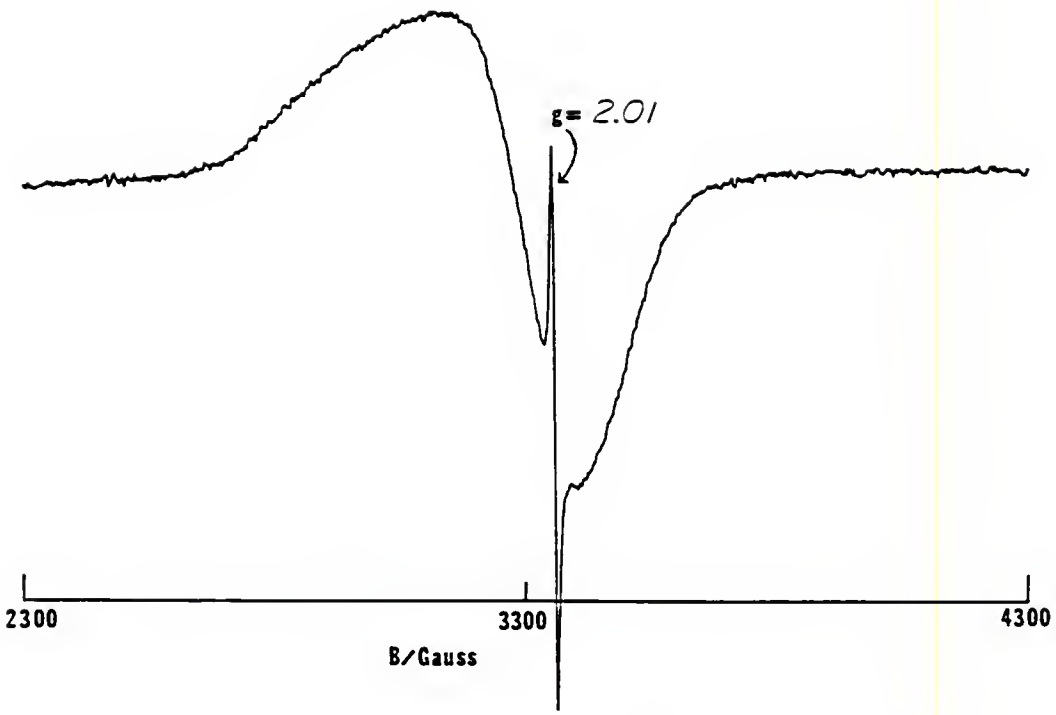


Figure 2-2. An EPR Spectrum of a Heterogeneous Acid Catalyst Before Complete Reaction.

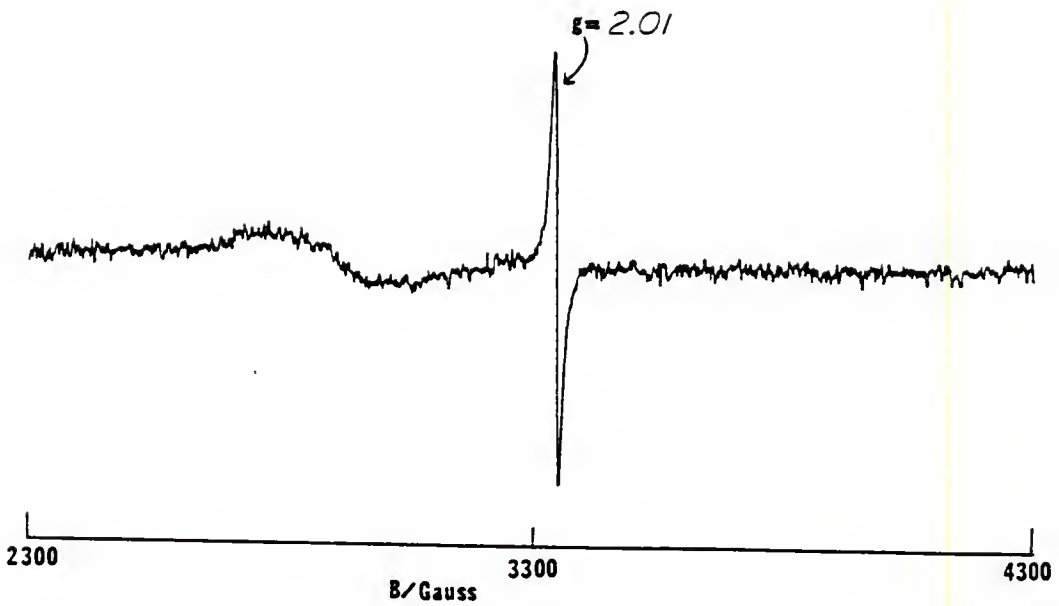


Figure 2-3. An EPR Spectrum of a Heterogeneous Acid Catalyst After Complete Reaction.

Preparation of a High-Silica Zeolite Catalyst Doped with Aluminum Chloride Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 10.0 grams of zeolite (dried at 250°C under vacuum) and 150 mL of carbon tetrachloride (dried over 4 A sieves). After purging the system with nitrogen (N_2), 5.0 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 5 days in the absence of light.

After approximately 1 hour the mixture developed a bright yellow color. After 2 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate had a slight yellow color and the resulting solid product obtained was bright yellow in appearance.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.012.

Preparation of a Y-Zeolite Catalyst Doped with Aluminum Chloride Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 23.9 grams of zeolite (dried at 300°C under vacuum) and 250 mL of carbon tetrachloride (dried over 4 A sieves). After purging the system with nitrogen (N_2), 13.29 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 2 days in the absence of light.

After approximately 1 hour the mixture developed a tan color. After 2 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate had a pale brown color and the resulting solid product obtained was tan in appearance. The catalyst was water-sensitive and turned white on exposure to moisture.

Preparation of a Boron Oxide Catalyst Doped with Aluminum Chloride Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 15.0 grams of boron oxide (dried at 80°C under vacuum) and 250 mL of carbon tetrachloride (dried over 4 A sieves). After purging the system with nitrogen (N_2), 7.50 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 3 days in the absence of light.

After approximately 1 hour the mixture developed a purple color. This color continued to increase in intensity until the mixture was black in appearance.

After 3 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was black in color.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.012.

Preparation of a Titanium Dioxide Catalyst Doped with Aluminum Chloride Using Carbon Tetrachloride as a Solvent

In a 500 mL 1-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 30.0 grams of titanium dioxide and 300 mL of carbon tetrachloride (dried over 4 A sieves). After purging the system with nitrogen (N_2), 15.0 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 3 days.

After approximately 1 hour the mixture developed a slight pink color which gradually increase in intensity until the mixture was peach in color.

After 3 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was peach in appearance.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.013.

Preparation of a Magnesium Oxide Catalyst Doped with Aluminum Chloride Using Carbon Tetrachloride as a Solvent

In a 250 mL 1-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 15.0 grams of magnesium oxide and 150 mL of carbon tetrachloride (dried over 4 A sieves). After purging the system with nitrogen (N_2), 7.5 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the

mixture was allowed to stir at reflux under a N_2 atmosphere for 3 days.

After approximately 1 hour the mixture developed a slight pink color which gradually increase in intensity until the mixture was bright pink in color.

After 3 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was pink in appearance.

The catalyst was water-sensitive and turned white on exposure to moisture.

Preparation of a Silica Gel Catalyst Doped with Aluminum Chloride Using Chloroform as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 10.20 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs) and 150 mL of chloroform (dried over 4 A sieves). After purging the system with nitrogen (N_2), 5.10 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 5 days.

After approximately 1 hour the mixture developed a purple color. This color continued to increase in intensity until the mixture was black in appearance.

After 5 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was burgundy in color.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.012.

Preparation of a Silica Gel Catalyst Doped with Aluminum Chloride Using Methylene Chloride as a Solvent

In a 500 mL 1-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 10.16 grams of silica gel and 200 mL of methylene chloride (dried over 4 A sieves). After purging the system with nitrogen (N_2), 5.07 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 5 days.

After 5 days the light purple reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was light purple in appearance.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.012.

Preparation of a Silica Gel Catalyst Doped with Aluminum Chloride Using 1,2-Dichloroethane as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 5.00 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs) and 175 mL of 1,2-dichloroethane (dried over 4 A sieves). After purging the system with nitrogen (N_2), 2.50 grams of

anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 5 days.

After approximately 1 hour the mixture developed a purple color. This color continued to increase in intensity until the mixture was black in appearance.

After 5 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was burgundy in color.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.012.

Preparation of a Silica Gel Catalyst Doped with Aluminum Chloride Using n-Hexane as a Solvent

In a 500 mL 1-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 10.16 grams of silica gel and 200 mL of n-hexane (dried over 4 A sieves). After purging the system with nitrogen (N_2), 5.07 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 3 days.

After 3 days the bright yellow reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was yellow in appearance.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.011.

Preparation of a Silica Gel Catalyst Doped with Aluminum Chloride Using Cyclohexane as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 5.00 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs) and 175 mL of cyclohexane (dried over 4 A sieves). After purging the system with nitrogen (N_2), 2.50 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 16 hours.

After 16 hours the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was light yellow in color.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.012.

Preparation of a Silica Gel Catalyst Doped with Aluminum Chloride Using Benzene as a Solvent

In a 1000 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 100 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs) and 750 mL of benzene (dried over 4 A sieves). After purging the system with nitrogen (N_2), 50 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 2 days.

After 2 days the reaction mixture was filtered under an N_2

atmosphere. The filtrate was colorless and the resulting solid product obtained was black in color.

The catalyst was water-sensitive and turned white on exposure to moisture. The catalyst gave a sharp EPR signal, similar to Figure 2-3, indicative of a free-radical with a g value of 2.012.

Preparation of a Silica Gel Catalyst Doped with Aluminum Chloride by Vapor Deposition

In a sublimation apparatus 3 grams of aluminum chloride and 5 grams of silicon dioxide (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs) were physically mixed and heated under vacuum at 240°C to sublimed the aluminum chloride through the support. After all of the aluminum chloride was removed from the sample the support was heated to 350°C to remove any excess aluminum chloride.

The same procedure was also repeated using alumina as the support material.

Preparation of a Palladium (II) Chloride-Aluminum Chloride Doped Catalyst Using Carbon Tetrachloride as a Solvent

In a 200 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 5.0 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs), 0.06 grams palladium (II) chloride ($PdCl_2$) and 100 mL of carbon tetrachloride (dried over 4 A sieves). The reaction mixture was stirred and heated at reflux under a nitrogen (N_2) atmosphere for 6 hours. Next 2.61 grams of anhydrous aluminum chloride

(Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 2 days.

After 2 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was orange in color.

The catalyst was water-sensitive and turned light peach on exposure to moisture.

Preparation of a Rhodium (III) Chloride-Aluminum Chloride Doped Silica Gel Catalyst Using Carbon Tetrachloride as a Solvent

In a 200 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 9.0 grams of a 2% rhodium (III) chloride ($RhCl_3$) on silica gel (prepared as above for palladium), 5.0 grams aluminum chloride, and 150 mL of carbon tetrachloride (dried over 4 A sieves).The reaction mixture was allowed to stir at reflux under a N_2 atmosphere for 24 hours.

After 24 hours the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was orange in color.

The catalyst was water-sensitive and turned light orange on exposure to moisture.

Procedure for the Adsorption of Pyridine onto Supports and Solid Acid Catalysts for the Characterization of Acid Sites

The infrared spectra of pyridine on solid acid catalysts has long been used for characterization of the acid sites on solid acid catalysts.[16,17,20-25] The procedure used to adsorb and desorb

pyridine was similar to that reported previously[16,17] with the exception that our samples were in powder form and not in pressed wafers. This meant that quantitative infrared measurements of the acid site concentrations could not be performed and only a qualitative determination of the nature of the acid sites could be made. Support and catalysts samples were dried at 200°C for 8 hours under vacuum prior to the adsorption experiments. Pyridine vapors were be contacted with the catalyst at room temperature for 2 to 3 hours and then the catalyst was placed under vacuum to remove any excess pyridine (2-3 hours). A sample of the support or catalyst was removed and a fluorolube mull prepared. An IR spectrum was obtained in the region from 1700 cm^{-1} to 1400 cm^{-1} in order to characterize the type of acid sites present. The sample was then evacuated at 150°C, 225°C and 300°C for 2 to 3 hours at each temperature. An IR spectrum was obtained after evacuation at each temperature. The results of these experiments are discussed in a later section.

Procedure for the Spin Trapping of Radicals on Solid Acid Catalysts Using DMPO

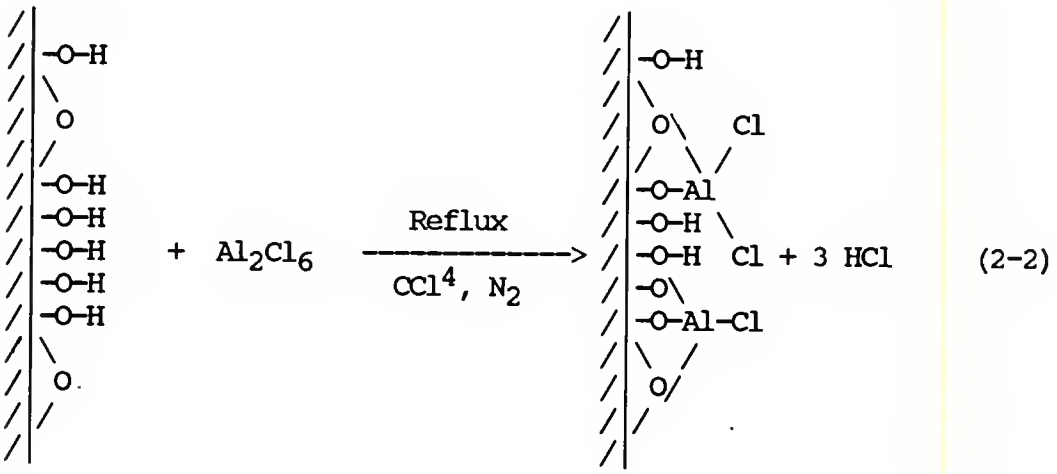
All manipulations were conducted in an inert atmosphere box. Powder samples of the catalysts were added to quartz EPR tubes that contained carbon tetrachloride or toluene. An amount of DMPO was added to this mixture that corresponded to the number of moles of aluminum chloride contained in the sample. The EPR spectra were collected in the usual manner. Computer simulations of the spin trapped radicals were performed using the program QPOW[38,39] as

modified by J. Telser[40] and N.M. Wong of the University of Florida, Gainesville, Florida.

2.3 RESULTS AND DISCUSSION

Preparation of a New Solid Acid Catalyst

As described in the experimental section the catalysts are prepared by the reaction of the hydroxyl groups of an inorganic oxide with aluminum chloride (Al_2Cl_6) in refluxing carbon tetrachloride (CCl_4), Equation 2-2. The reaction of aluminum chloride with silicon



(2-2)

dioxide was monitored by accurately weighing the aluminum chloride and silicon dioxide before the reaction. When the weight of the resulting aluminum chloride doped silica gel was subtracted from the sum of the weights of the starting materials used in the reaction it was determined that 1.1 moles of hydrogen chloride (HCl) was evolved for every mole of $AlCl_3$ used. This suggests that over 90% of the chloroaluminum species on the catalyst surface of this support has

the composition $(-O-)AlCl_2$. Since the average composition is two chlorides per aluminum and Al_2Cl_6 would sublime off upon heating (which does not occur) there is very little $(-O-)_2AlCl$ present. A blank reaction between SiO_2 and CCl_4 showed no HCl evolution and the resulting solid did not have any acidic properties as indicated by pyridine adsorptions. This result is consistent with literature reports in that CCl_4 does not chlorinate the surface of silica gel below a temperature of 350°C.[41]

Past attempts[8] conducted on this reaction have employed solvents other than CCl_4. It has been determined that chloroform, methylene chloride, ethylene dichloride and saturated hydrocarbons (to name a few) do not product a solid acid catalyst with the properties described for a solid acid prepared in CCl_4.[15] Several patents have been issued for the treatment of inorganic oxides with aluminum chloride to form strong acid catalysts.[5,8-14] In each of these cases aluminum chloride is rapidly evolved from the surface and only short term activity results.[4,5,8-14] This is in contrast with what has been found for the aluminum chloride doped inorganic oxides prepared in CCl_4.

The new catalysts reported in the experimental section have been characterized by IR spectroscopy, solid-state MAS NMR spectroscopy and calorimetric titration. As detailed in latter sections these aluminum chloride doped inorganic oxides are catalysts for a wide range of acid catalyzed reactions.

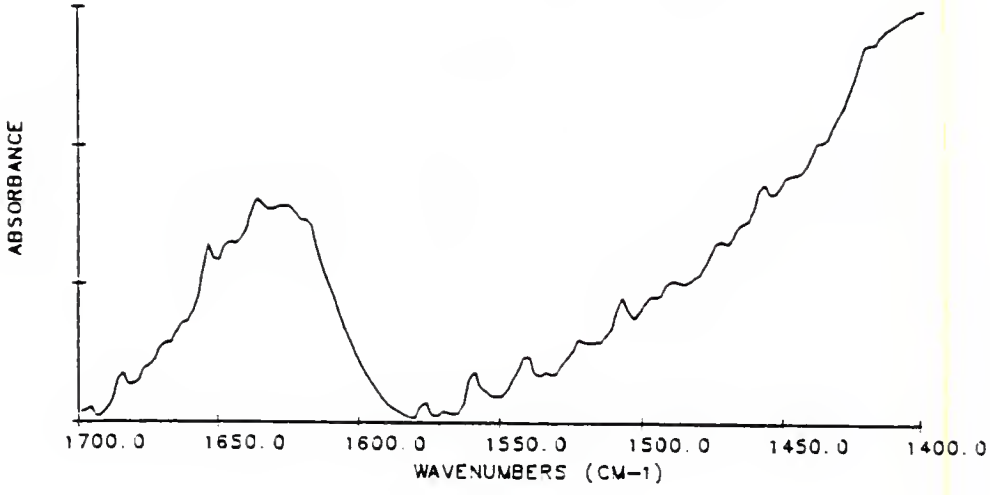


Figure 2-4. Infrared Spectrum of SiO_2 Dried at 200°C.

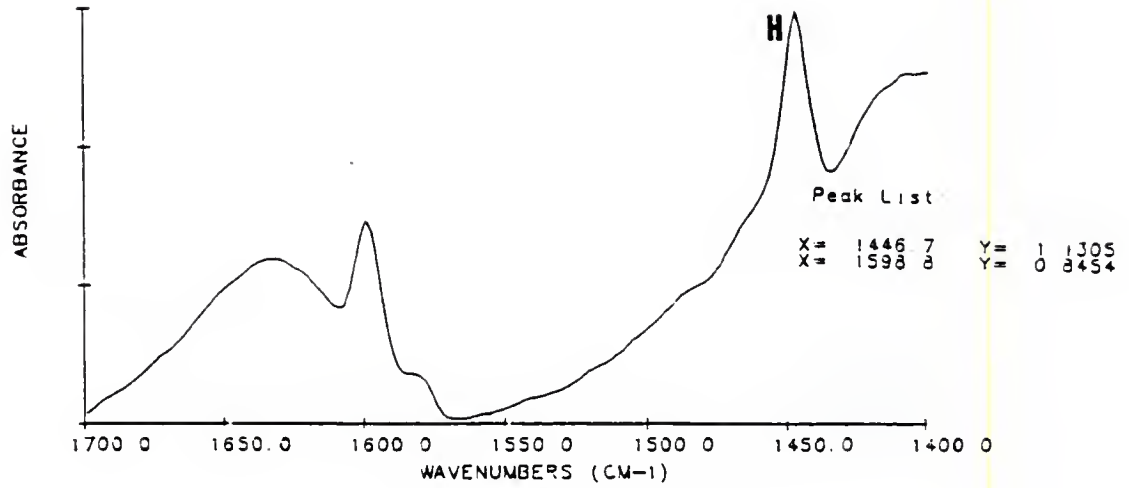


Figure 2-5. Infrared Spectrum of SiO_2 After Pyridine Adsorption and Evacuation at Room Temperature.

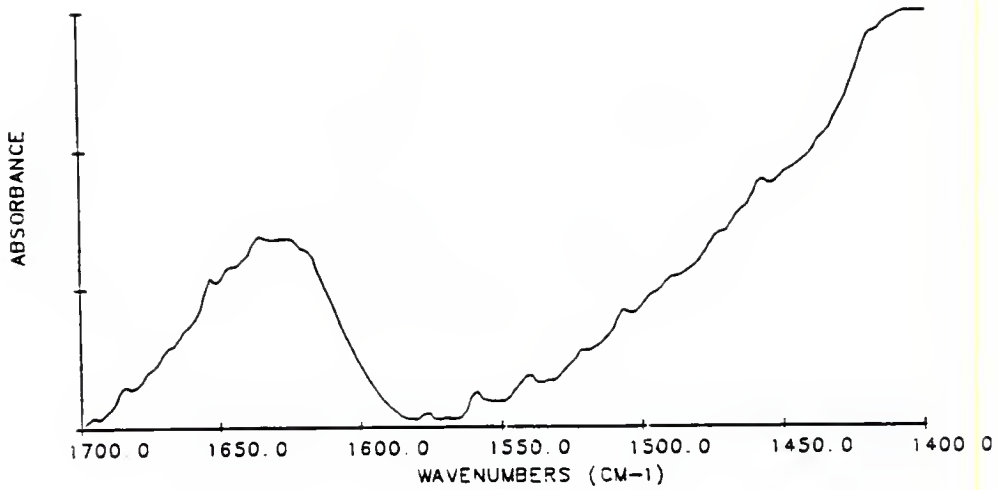


Figure 2-6. Infrared Spectrum of SiO_2 After Pyridine Adsorption and Evacuation at 150°C.

Characterization of the New Solid Acid Catalysts by the Infrared Spectroscopy of Adsorbed Pyridine

Using the procedure outlined in the experimental section a sample of the silicon dioxide was dried under vacuum at 200°C for 8 hours and three IR spectra were collected. The three IR spectra are shown in Figures 2-4 to 2-6. The IR spectrum shown in Figure 2-4 is of the silicon dioxide after drying at 200°C under vacuum. This relatively featureless spectrum is typical of the inorganic oxides used. After pyridine is adsorbed onto the silica gel surface and all excess pyridine is removed by evacuation at room temperature, two bands that are indicative of hydrogen bonded pyridine appear, Figure 2-5. The band at 1447 cm^{-1} is attributed to the interaction of pyridine with the hydroxyl groups of the silica gel and results from hydrogen bonding since it is known that unmodified silicon dioxide has no strong acidic or basic properties.[16,19] This band is located at 1438 cm^{-1} for free pyridine. When the silicon dioxide is evacuated at 150°C all of the adsorbed pyridine is removed indicating that the pyridine interacts only weakly with the surface of the support, (see Figure 2-6). The results obtained on the silicon dioxide material parallel the results obtained by Parry[16] for silicon dioxide and indicates that the experimental method being used is valid.

Next a sample of the silicon dioxide doped with Al_2Cl_6 ($AlCl_3/SiO_2$) which had been prepared in CCl_4 was dried at 200°C for 8 hours. The infrared spectrum of the dried $AlCl_3/SiO_2$ is similar to the IR spectrum of the dried silicon dioxide, Figure 2-7. When pyridine is adsorbed onto the $AlCl_3/SiO_2$ catalyst and evacuated at

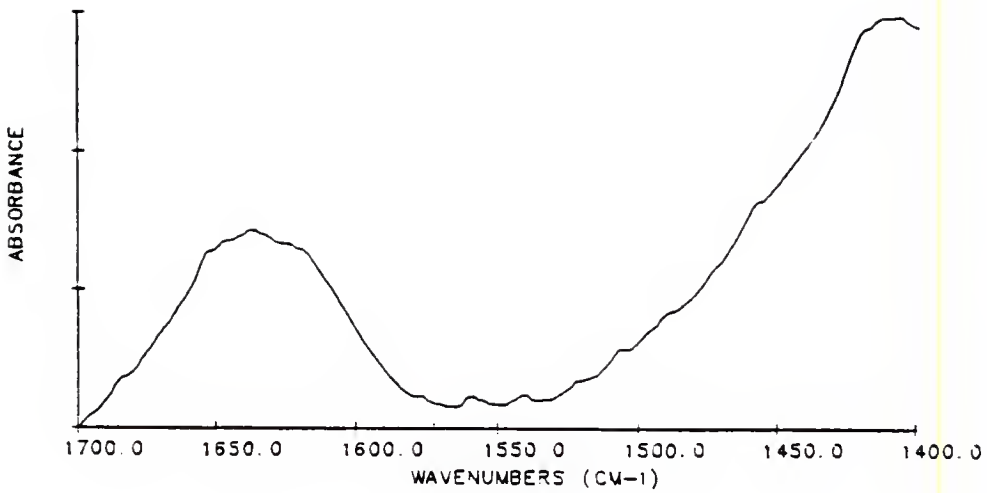


Figure 2-7. Infrared Spectrum of $AlCl_2$-SiO_2 Dried at 200°C.

room temperature, bands indicative of both Bronsted and Lewis acid sites are observed, Figure 2-8. The large band at 1540 cm^{-1} results from pyridinium ion which is formed by the protonation of pyridine by Bronsted acid sites. Lewis acid sites are indicated by the presence of a band at 1449 cm^{-1}. Since the IR spectrum is obtained after evacuation at room temperature, there is some hydrogen bonded pyridine present on the surface and is responsible for the broad shape of the Lewis acid band. The peak at ~1499cm^{-1} is a band present in both Bronsted and Lewis acid bound pyridine and cannot be used to distinguish between the two types of acid sites[16]. After evacuation at 150°C, to remove any hydrogen bound pyridine, the peak for the Lewis acid bound pyridine is centered at 1456 cm^{-1}, Figure 2-9. This is a shift of 18 cm^{-1} and is comparable to shifts reported in the literature for solid acid cracking catalysts.[16] In addition to a shift in the Lewis acid band for pyridine there is a large amount of Bronsted acid sites present as indicated by the band at 1540 cm^{-1}. Even after evacuation at 300°C both Bronsted and Lewis acid sites are present indicating a very strong interaction between the surface of the solid acid and the adsorbed pyridine, Figure 2-10. The results for this catalyst are in good agreement with the data obtained by Parry[16] and other workers in the area[17] for commercial amorphous silica-aluminas and zeolites. A summary of the infrared shift data for pyridine adsorbed onto various aluminum chloride treated inorganic oxides ($AlCl_2$-X; X= inorganic support) is presented in Table 2-1.

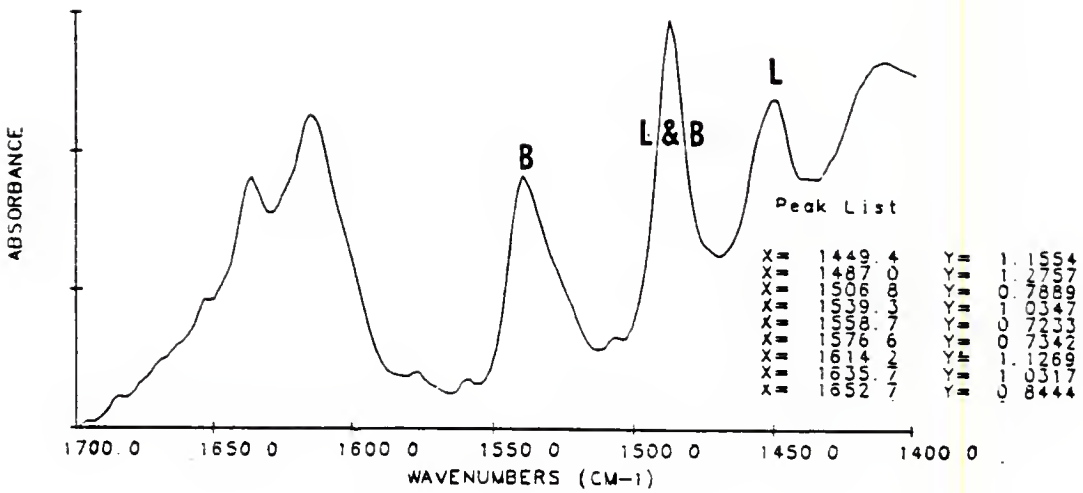


Figure 2-8. Infrared Spectrum of $AlCl_2$-SiO_2 After Pyridine Adsorption and Evacuation at Room Temperature.

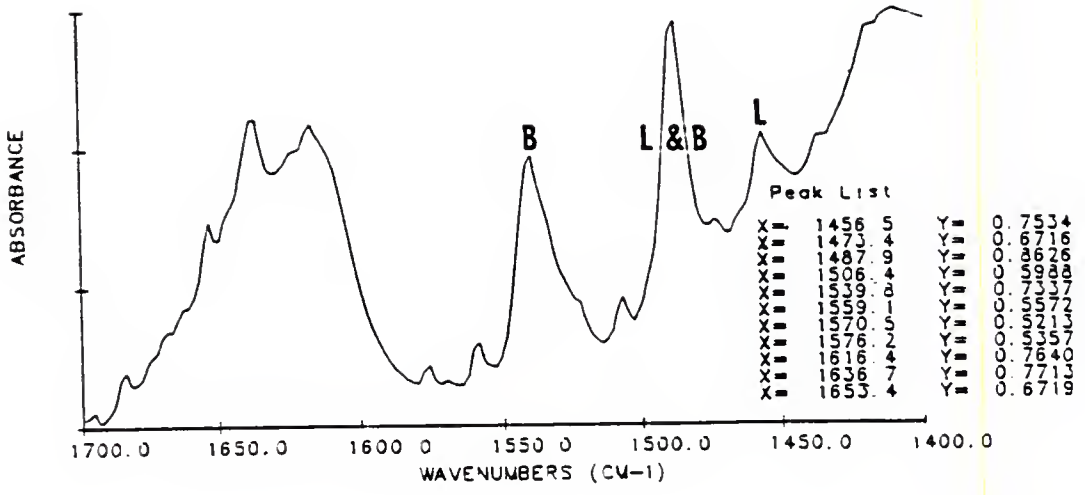


Figure 2-9. Infrared Spectrum of $AlCl_2$-SiO_2 After Pyridine Adsorption and Evacuation at 150°C.

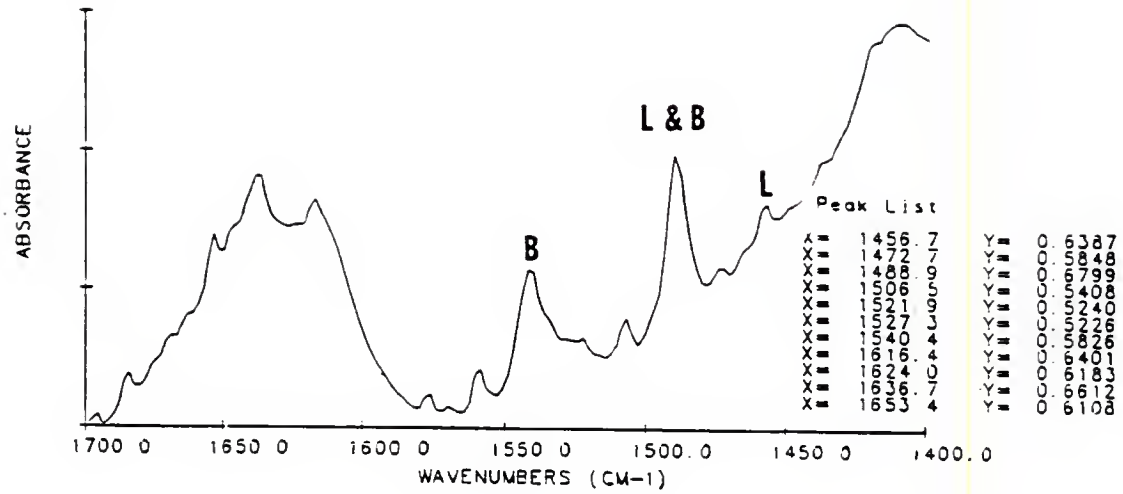


Figure 2-10. Infrared Spectrum of $AlCl_2$-SiO_2 After Pyridine Adsorption and Evacuation at 300°C.

Table 2-1. Infrared Shift Data for Pyridine Adsorbed onto $AlCl_2$-X Catalysts.

X	SOLVENT*	SHIFT OF LEWIS BAND**
SiO_2	CCl_4	18.0
Al_2O_3	CCl_4	15.2
Silicalite***	CCl_4	18.1
B_2O_3	CCl_4	18.1
TiO_2	CCl_4	14.1
MgO	CCl_4	7.8
SiO_2	$CHCl_3$	9.3
SiO_2	CH_2Cl_2	8.6
SiO_2	C_6H_{14}	8.9
SiO_2	C_6H_6	8.3

* This solvent was used to prepare the catalyst.

** This shift is measured after pumping at 150°C on the sample exposed to pyridine. The free pyridine band occurs at 1438.5 cm^{-1}.

*** A high silica zeolite.

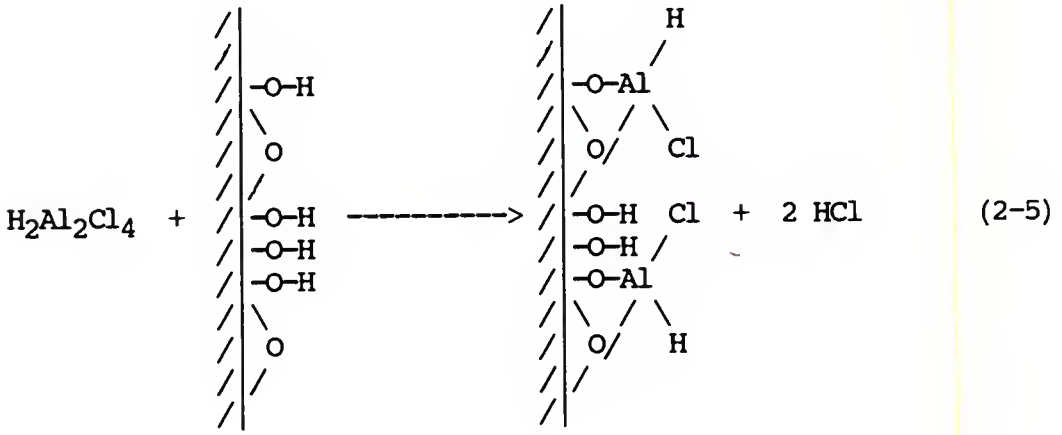
As seen in Table 2-1 the acid treated SiO_2, silicalite and B_2O_3 supports resulted in the largest shifts for the Lewis acid band. Alumina and titanium dioxide exhibited shifts in an intermediate range with magnesium oxide resulting in the lowest shift. The frequency shifts listed are after evacuation at 150°C to remove any weakly hydrogen bound pyridine. The low shift for MgO is not unexpected due to the fact that magnesium oxide is basic[19] and the resulting material formed from reacting a strong acid with a base would result in a product that is weakly acidic in nature. Even though the shift in the Lewis acid band for the MgO catalyst issmall and in the range that would normally represent hydrogen bonded pyridine, the band is still present after evacuation at 150°C and considered to arise form a Lewis acid-base interaction.

Several catalysts were prepared by methods described in the patent literature and the results of the pyridine adsorptions are listed at the bottom of Table 2-1. All patented catalysts that were used employed silicon dioxide as the support material and solvents other than CCl_4. For each of the solvents used a shift of only 8 or 9 cm^{-1} was observed after evacuation at 150°C. An explanation for the decrease in frequency shifts upon changing from carbon tetrachloride to other solvents may be that each of the other solvents contain reactive hydrogens or are basic molecules. It is well known that aluminum chloride can react with organic compounds to form ionic complexes as shown in Equations 2-3 and 2-4.[42] When solvents such as chloroform, methylene chloride and saturated

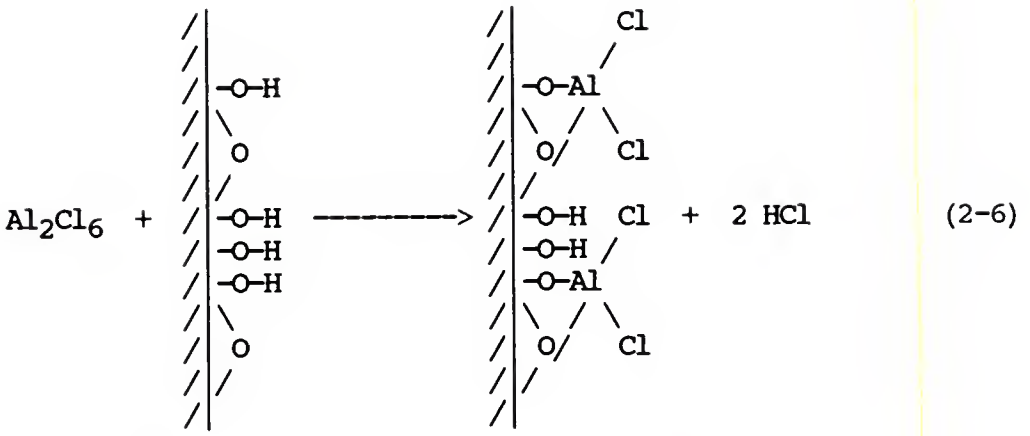
$$2\ R\text{-}H + Al_2Cl_6 \longrightarrow 2\ R^+HAlCl_3^- \qquad (2\text{-}3)$$

$$2\ R\text{-}Cl + Al_2Cl_6 \longrightarrow 2\ R^+AlCl_4^- \qquad (2\text{-}4)$$

hydrocarbons are employed, the aluminum chloride can react with the solvent to form halo organo-aluminum complexes.[42] For solvents with available hydrogens the reaction that may then take place is abstraction of a hydride ion from the organic halide generating an aluminum hydride and a carbonium ion.[43] The carbonium ion may abstract a hydride ion from another solvent molecule or the support material forming a neutral species. The aluminum hydride complex may react with the support material, liberating HCl and forming a chloroaluminum hydride complex. This species is less acidic than the chloroaluminum species formed when pure Al_2Cl_6 is reacted with the support material, Equations 2-5 and 2-6. Many other reactions are possible between the aluminum chloride and the reaction medium. The point to be made is that in solvents that contain carbon-hydrogen



(2-5)



(2-6)

bonds reactions involving aluminum-chlorine bonds that result in the decomposition of the aluminum chloride into aluminum hydride or organo-aluminum species that would exhibit lower acidity than aluminum chloride alone may occur[43,44]. A reason for the decrease in acidity for the catalyst prepared in benzene is that benzene is a good π-base and would form an acid-base complex with the aluminum chloride. The complexed aluminum chloride would be a weaker acid than the free aluminum chloride. On the other hand, a fully chlorinated solvent such as carbon tetrachloride will undergo an exchange of chloride ion with aluminum chloride and will result in no net reaction, Equations 2-7 to 2-9.

$$2\ Cl_3CCl + Al_2Cl_6 \longrightarrow 2\ Cl_3C^+AlCl_4^- \qquad (2\text{-}7)$$

$$2\ Cl_3C^+AlCl_4^- \longrightarrow 2\ Cl_3CCl + Al_2Cl_6 \qquad (2\text{-}8)$$

$$2\ Cl_3CCl + Al_2Cl_6 \longrightarrow 2\ Cl_3CCl + Al_2Cl_6 \qquad (2\text{-}9)$$

The result of this reaction is that the aluminum chloride is stabilized in solution by the carbon tetrachloride. Since the aluminum chloride cannot react with the solvent the aluminum chloride is forced to react with the hydroxyl groups of the support material.

The trend for the frequency shifts of the Lewis acid band for pyridine can be clearly seen in Table 2-1. A neutral support such as silica gel exhibits the highest shift along with a high silica zeolite and boron oxide (B_2O_3). Acidic supports such as alumina and titanium dioxide have the next largest shifts and the basic support magnesium oxide exhibits the lowest frequency shift. An explanation involving the acidic or basic properties of each support would be acceptable except that boron oxide is not a neutral support. Boron oxide has a structure which contains trigonal BO_3 units and has the same acidic properties.[45] Because of the acidity associated with boron oxide it would be expected that boron oxide would exhibit a frequency shift for Lewis acid bound pyridine similar to that exhibited by alumina. It should be stated that the same Lewis acid is used to treat each support and would not be the controlling factor in determining the frequency shift of the Lewis acid bound pyridine if the support was not interacting with the acid center.

The shift in the Lewis acid band is a result of an inductive effect involving the donation of the nitrogen lone pair of the pyridine to a vacant orbital on a Lewis acid such as aluminum trichloride ($AlCl_3$). As electron density is drawn away from the nitrogen the $p\pi$-$p\pi$ interaction between the ring carbons increases

resulting in an increase in the ring bending frequency for pyridine. It has been previously reported that as the strength of the Lewis acid increases the Lewis acid band for pyridine will shift to higher frequencies.[16] This is a direct result of the increased electron withdrawing strength of the Lewis acid. In the case of the inorganic oxides treated with aluminum chloride, the strength of the chloroaluminum center resulting from aluminum chloride should be the same for each oxide. A difference in the electron withdrawing strength of the acids would arise from the electronegativity of the oxides themselves.

The Pauling electronegativity values for each of the elements in the inorganic oxides are as follows: boron= 2.0, silicon= 1.8, aluminum= 1.5, titanium= 1.5 and magnesium= 1.2.[46] This trend in electronegativities (Pauling and Mulliken) correlates with the trend in the frequency shifts of the Lewis acid bound pyridine and may contribute to the observed trend in the acid strengths. The trend in the activities of these materials for the catalytic cracking of hydrocarbons will be discussed in greater detail in a later section.

Characterization of a New Solid Acid Catalyst by ^{27}Al and ^{29}Si Solid-State Magic Angle Spinning (MAS) FT NMR Spectroscopy

The following discussion is concerned with the solid-state MAS NMR spectra of the inorganic oxide treated with aluminum chloride as described in the experimental section of this chapter.

The first material examined was a catalyst which had been prepared by refluxing SiO_2 and Al_2Cl_6 in CCl_4 with enough water present to hydrolyze all the Al_2Cl_6 in order to determine the

spectrum of a decomposed catalyst. If a catalyst were prepared in the presence of water or a good catalyst is exposed to water, it would be expected that the aluminum chloride would be hydrolyzed and form a 6-coordinate aluminum species. The catalyst prepared in the presence of water (Figure 2-11) shows only one aluminum peak centered at 0 ppm for the ^{27}Al MAS NMR , which is indicative of 6-coordinate aluminum. Figure 2-12 (which is referenced to TMS) shows the ^{29}Si MAS NMR for the catalyst prepared in the presence of water and indicates that there is only one type of silicon present which is the 4-coordinate silicon of silicon dioxide. The broad peak centered at -110 ppm relative to TMS is consistent with reports in the literature for the ^{29}Si MAS NMR of silica gels and silicalite (which is an all silicon zeolite).[29] No other peaks have developed from the formation of Al-O-Si bonds by the reaction of aluminum chloride. The aluminum chloride has simply been hydrolyzed and for the most part is a weakly associated 6-coordinate species on the SiO_2 surface. The slight broadening of the ^{29}Si peak compared to unmodified SiO_2 could be the result of weak association with these aluminum species. Another factor that will contribute to the peak broadening is that not all silicons are bonded together by oxygen bridges (Si-O-Si) in silica gel. On the surface of the silica gel the silicon dioxide lattice terminates in Si-O-H (silanol) groups whose chemical shift is approximately 1 ppm different from that of groups in the bulk lattice.[29]

The next material examined was a catalyst which had been prepared by refluxing SiO_2 and Al_2Cl_6 in dry CCl_4 under an N_2

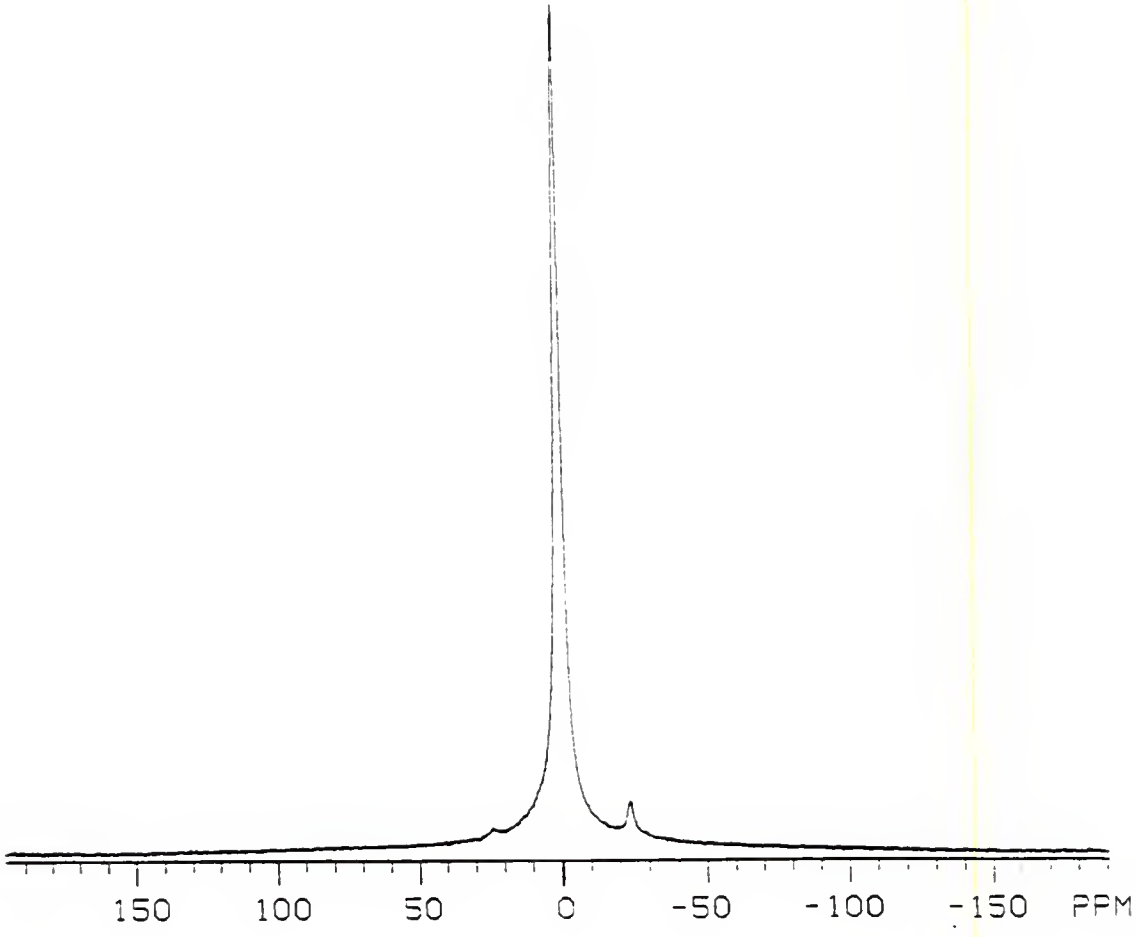


Figure 2-11. An ^{27}Al Solid-State NMR of an $AlCl_2$-SiO_2 Catalyst Prepared in the Presence of H_2O.

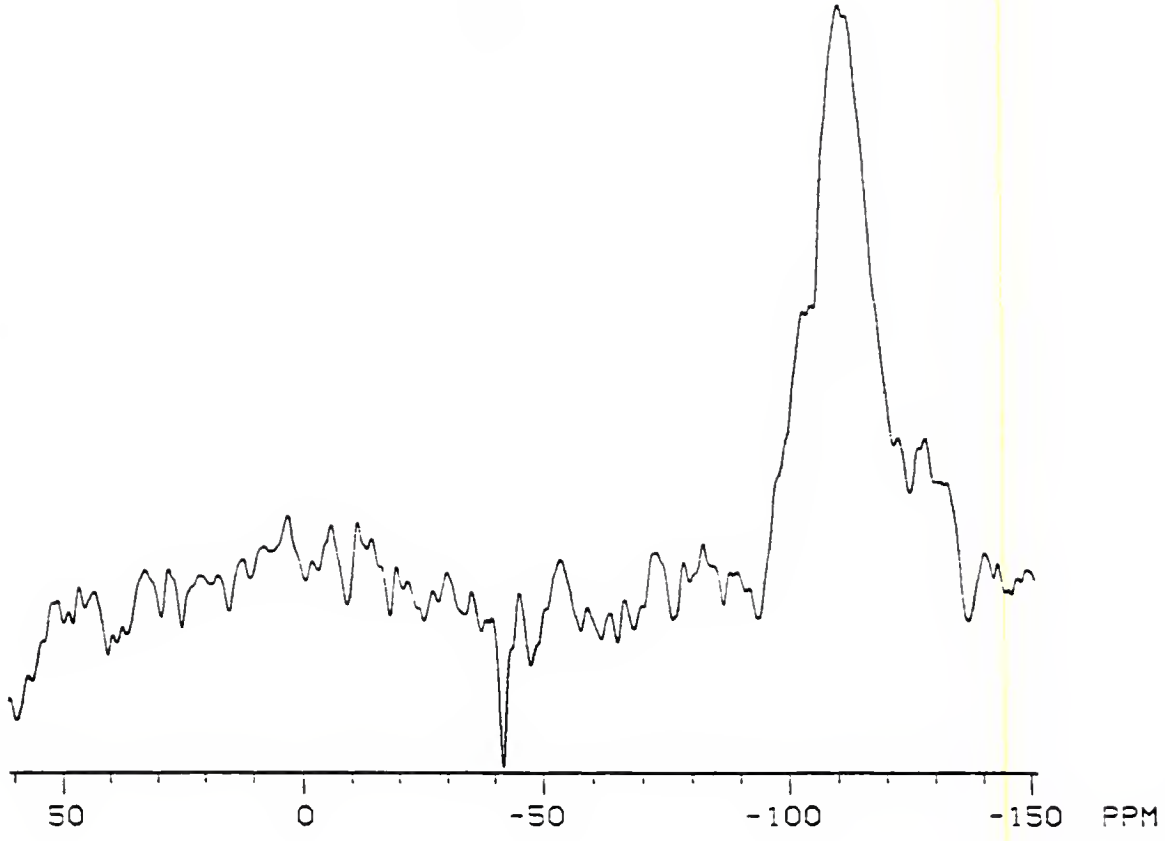
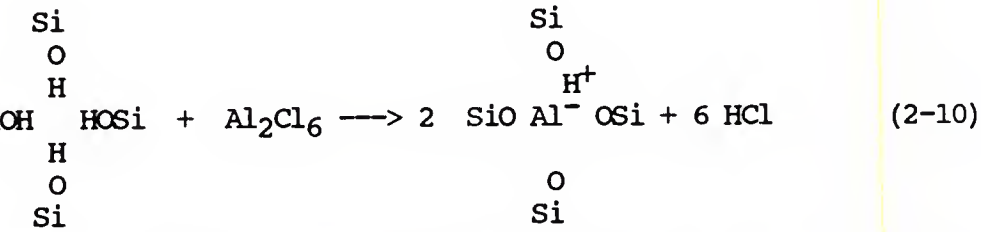


Figure 2-12. A ^{29}Si Solid-State NMR of an $AlCl_2$-SiO_2 Catalyst Prepared in the Presence of H_2O.

atmosphere. The ^{27}Al MAS NMR for an active catalyst (before catalysis) is shown in Figure 2-13. The peak at 0 ppm results from the presence of 6-coordinate aluminum which formed after the catalyst was exposed to water vapor in the air during the loading of the NMR tube. The peak centered at 55 ppm results from 4-coordinate aluminum, most likely with hydroxide ligands as well as Al-O-Si bonds. The peak at 55 ppm could also arise from the formation of zeolitic aluminum by addition of aluminum into a surface vacancy as shown in Equation 2-10.[33]



(2-10)

The peak at 65 ppm results from Si-O-$AlCl_2$ on the silica gel surface which would be consistent with the value of 62.8 ppm given for aluminum chlorohydrate with a ratio of Cl/OH of 2.5.[31]

When a high surface area silica gel is treated with aluminum chloride several types of tetrahedral aluminum centers are formed. Shown in Figure 2-14 is the ^{27}Al MAS NMR for a 690 m^2/gram silica gel treated with aluminum chloride. For the high surface area silica gel three distinct peaks are detected which are at 70, 52 and 23 ppm. The peak at 70 is assigned to a Si-O-$AlCl_2$ species which was observed for the 340 m^2/gram silica gel. The peak at 52 ppm most likely results from zeolitic or hydroxychloro [Si-O-AlCl(OH)]

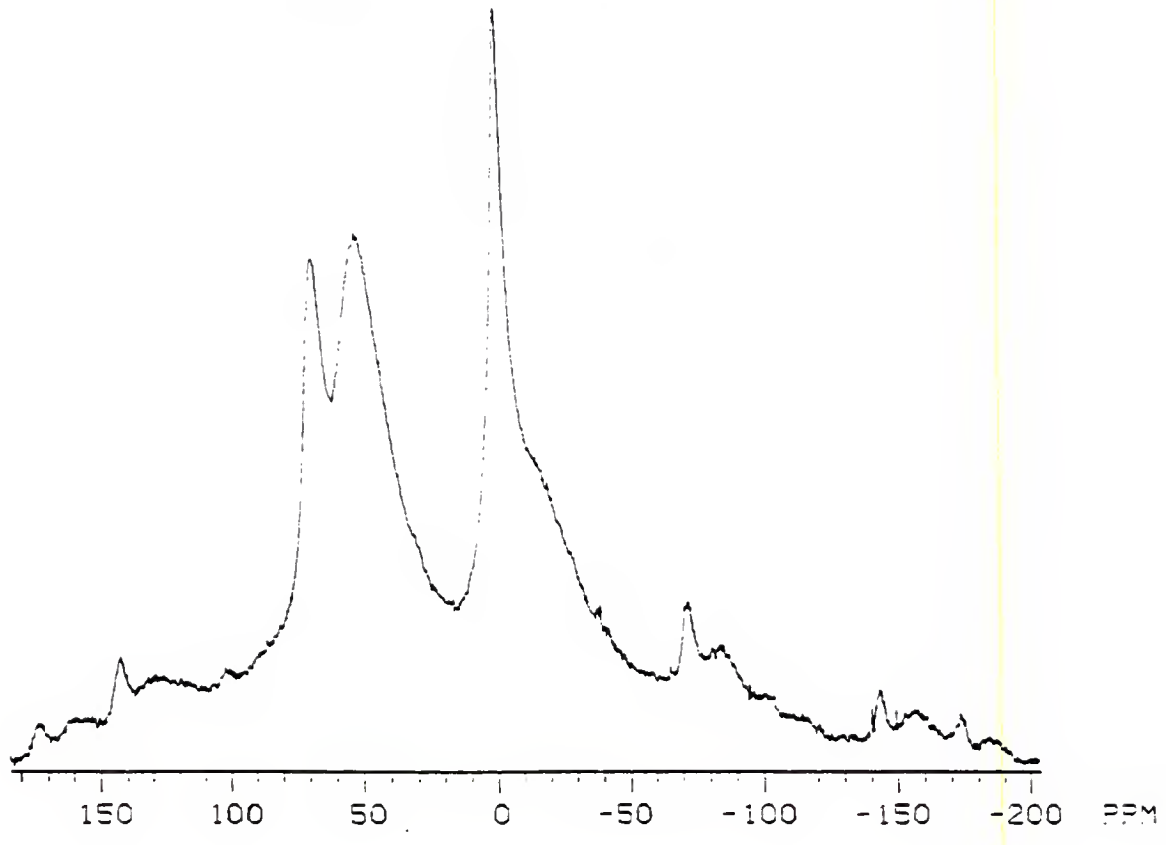


Figure 2-13. An ^{27}Al Solid-State NMR of an Active $AlCl_2$-SiO2 Catalyst Prepared in the Absence of H_2O.

aluminum centers and the peak at 23 ppm probably results from a chemisorbed 6-coordinate hydroxychloro aluminum species.

This may be explained using the stoichiometry of the catalyst preparation reaction. The aluminum chloride treated silica gel is normally prepared using a silica with a surface area of 340 m^2/gram and a hydroxyl group concentration of approximately 10 mmole/gram.[35,47] Since a 2:1 ratio by weight of inorganic oxide to aluminum chloride is used there are 7.5 mmole of $AlCl_3$ per gram of support which would yield roughly 80% coverage of the solid support. If the surface area of the support is doubled a corresponding increase in the concentration of hydroxyl groups would occur and the total coverage of the aluminum chloride would decrease to approximately 40%. This would mean that there would be, on average, 2.5 hydroxyl groups for every $AlCl_3$ molecule used in the reaction. According to this stoichiometry an average of two Al-Cl bonds would be hydrolyzed by the silica surface for every $AlCl_3$ molecule used in the reaction. The resulting ^{27}Al MAS NMR should then show a significant increase in the number of bands for hydrolyzed chloroaluminum species as in Figure 2-14.

Shown in Figure 2-15 is the ^{29}Si MAS NMR of the 690 m^2/gram silica gel reacted with aluminum chloride in CCl_4. In contrast to Figure 2-12 where only one peak was observed for the ^{29}Si MAS NMR, there are now at least two distinct peaks centered at -88 and -105 ppm. The peak at -105 ppm is due to the formation of one Si-O-Al bond per silicon atom on the silica surface and the peak at -88 ppm

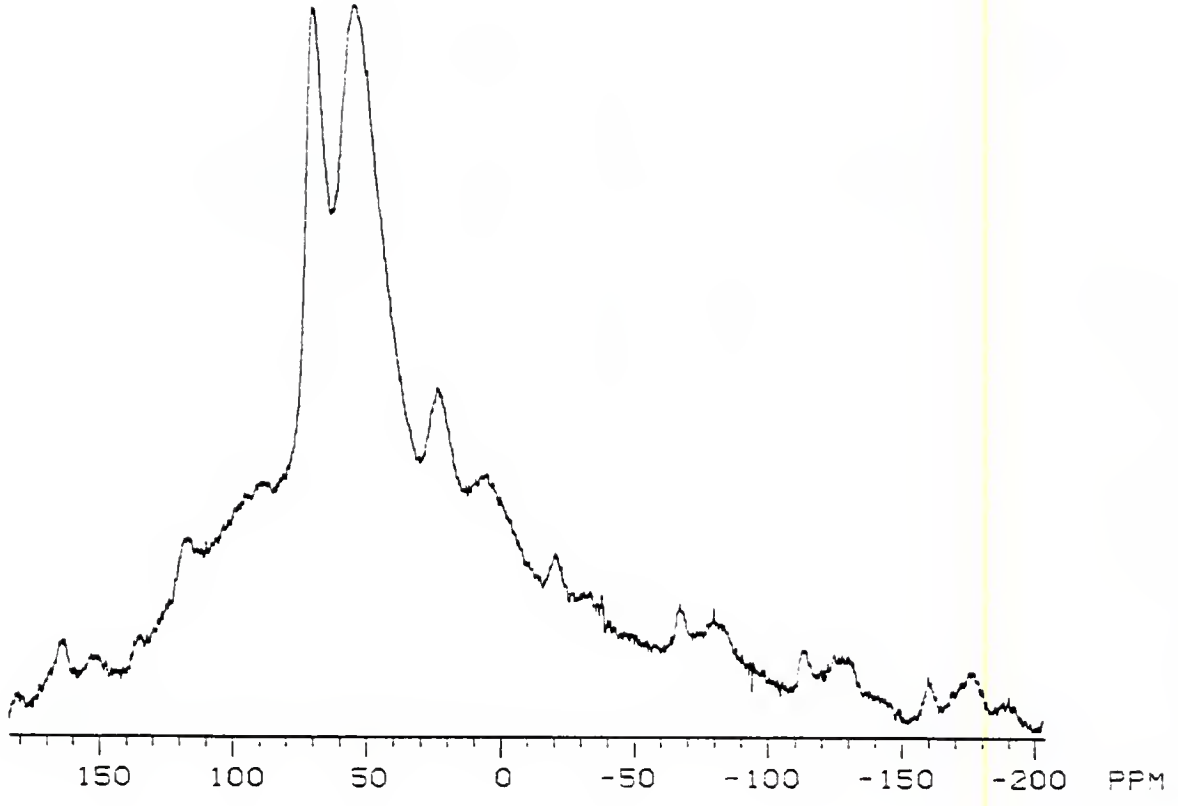


Figure 2-14. An ^{27}Al Solid-State NMR of an $AlCl_2$-SiO_2 Catalyst Prepared with a 690 m^2/gram Surface Area Silica Gel.

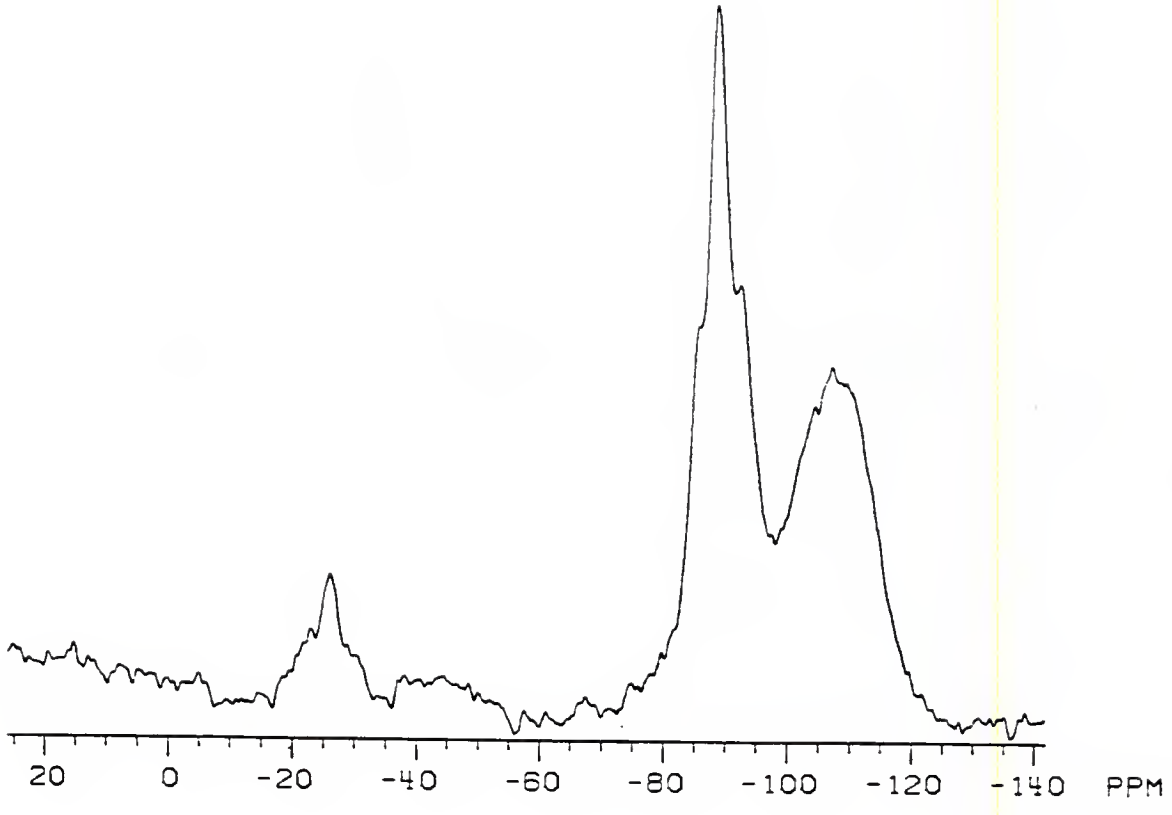


Figure 2-15. A ^{29}Si Solid-State NMR of an $AlCl_2$-SiO_2 Catalyst Prepared with a 690 m^2/gram Surface Area Silica Gel.

is due to the formation of two Si-O-Al bonds to one silicon center on the silica surface. These results are consistent with literature values given for amorphous silica-aluminas, aluminosilicates and zeolites.[29,30]

The presence of peaks ar -88 and -105 ppm are good evidence for the incorporation of aluminum chloride onto the silica surface and supports the fact that the aluminum chloride has actually been chemically bonded to the solid support. When the catalysts studied in Figures 2-14 and 2-15 are used in a catalytic cracking reaction (reported later in this section) low activities are observed. This may be the result of the increased amount of hydrolyzed chloroaluminum centers present on the catalyst surface. The activity that is observed may result from a low number of hydroxy chloro species and zeolitic aluminum centers which would only show high activities at high temperatures.[2,3]

The ^{27}Al and ^{29}Si MAS NMR spectra of a silica gel support which has been treated with excess Al_2Cl_6 (100 wt%) is shown in Figures 2-16 and 2-17. For the ^{27}Al MAS NMR a large peak at 105 ppm is observed which results from uncomplexed aluminum chloride and is in agreement with the shifts reported in the literature for the ^{27}Al solution NMR of Al_2Cl_6 and $AlCl_4^-$.[32] Peaks in the ^{27}Al MAS NMR are also observed at 38 and 0 ppm which result from the hydroxychloro aluminum species discussed earlier. The ^{29}Si MAS NMR spectrum of the same catalyst exhibits only one peak, resulting from the framework silicon dioxide[29], indicating that most of the aluminum chloride is on the support surface as Al_2Cl_6.

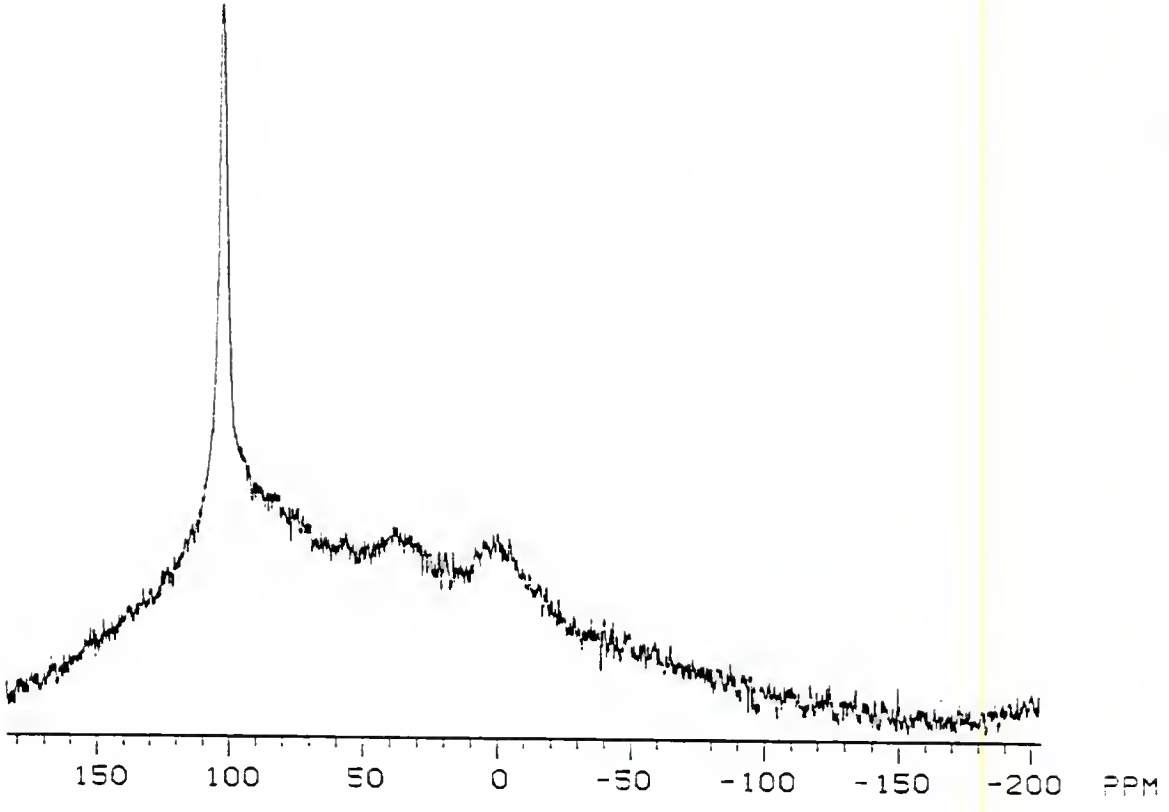


Figure 2-16. An ^{27}Al Solid-State NMR of an $AlCl_2$-SiO_2 Catalyst Prepared with 100 wt% of Aluminum Chloride.

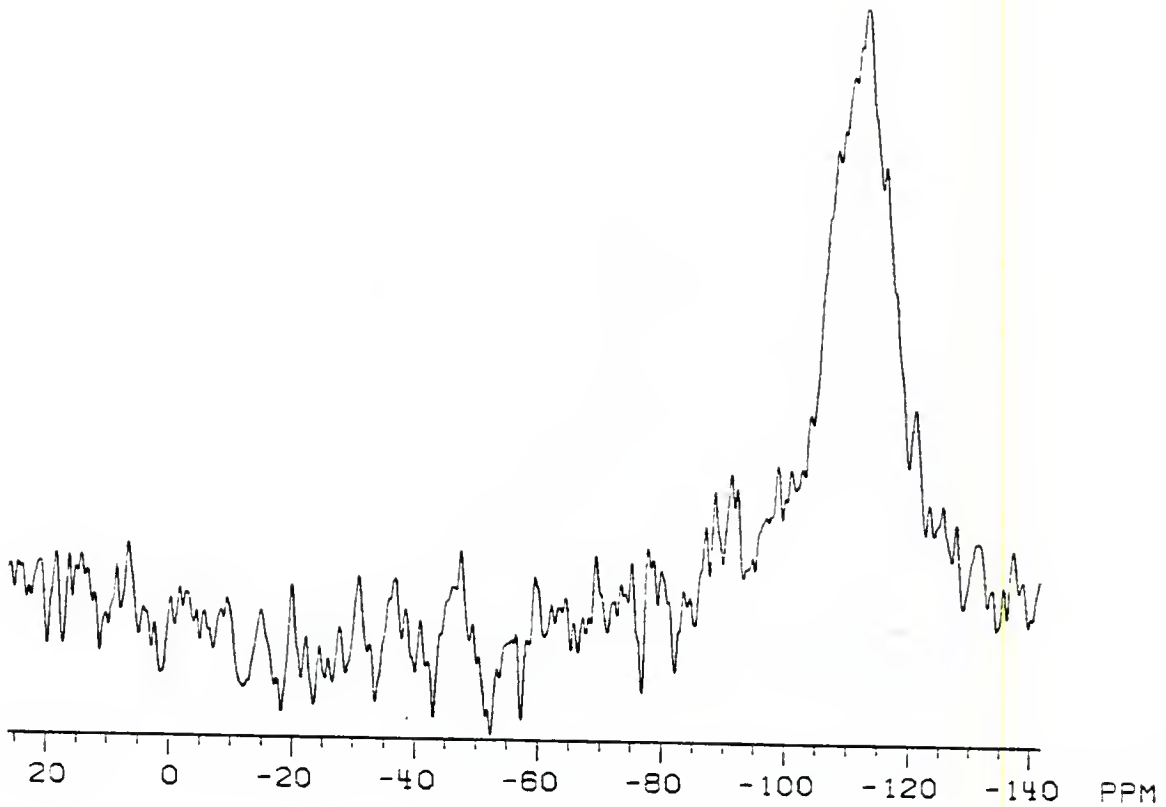


Figure 2-17. A ^{29}Si Solid-State NMR of an $AlCl_2$-SiO_2 Catalyst Prepared with 100 wt% of Aluminum Chloride.

The ^{27}Al and ^{29}Si MAS NMR spectra of a catalyst after use in a catalytic cracking reaction are shown in Figures 2-18 and 2-19. Once again in the ^{27}Al MAS NMR 6-coordinate and 4-coordinate aluminum centers are present with the 4-coordinate aluminum center giving a peak at ~70 ppm which would indicate the presence of an Si-O-$AlCl_2$ species. The oscillation in the ^{27}Al MAS NMR baseline is caused by some paramagnetic material (coke) which was deposited on the catalyst surface during catalysis. The ^{29}Si MAS NMR displays peaks for the framework silicon dioxide plus the silicon atoms associated with the formation of one Si-O-Al bond per silicon center. This indicates that even under catalytic conditions the tetrahedral chloroaluminum centers are stable and could be responsible for the catalytically active centers.

From the ^{27}Al and ^{29}Si MAS NMR data it has been determined that the catalyst prepared by reaction of aluminum chloride with aninorganic oxide results in a solid material which has tetrahedral chloroaluminum centers. The IR data for adsorbed pyridine indicates that both Bronsted and Lewis acid sites are present and the frequency shifts for the Lewis acid bound pyridine are comparable to those exhibited by conventional cracking catalysts.[16,17] As a result of these findings the new solid acid catalysts described in the experimental section of this chapter were used for various hydrocarbon conversion reactions.

The next section will deal with the characterization of the radical on the catalyst surface generated during the catalyst

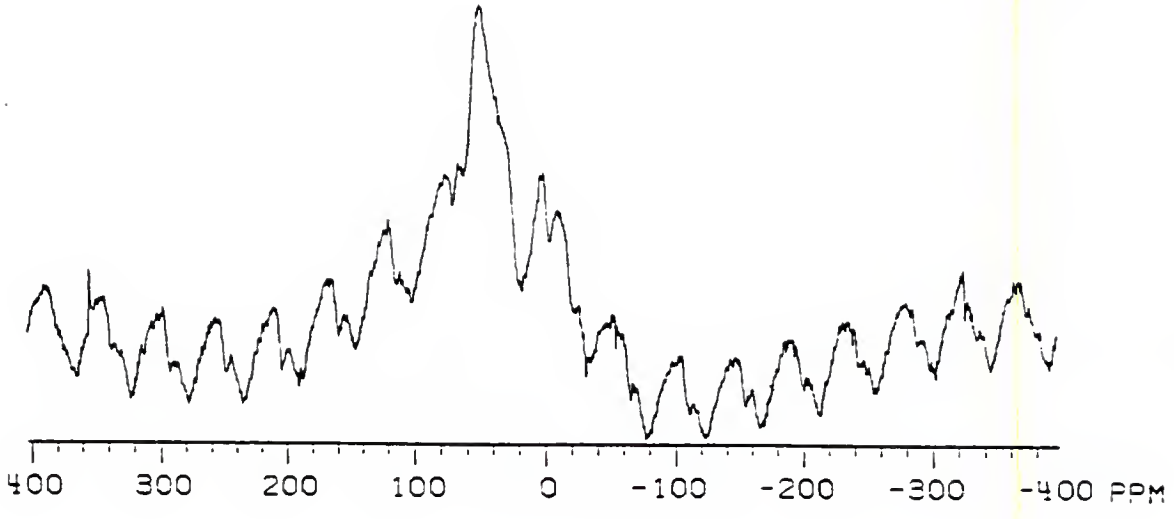


Figure 2-18. An ^{27}Al Solid-State NMR of an $AlCl_2$-SiO_2 Catalyst After Reaction with n-Pentane.

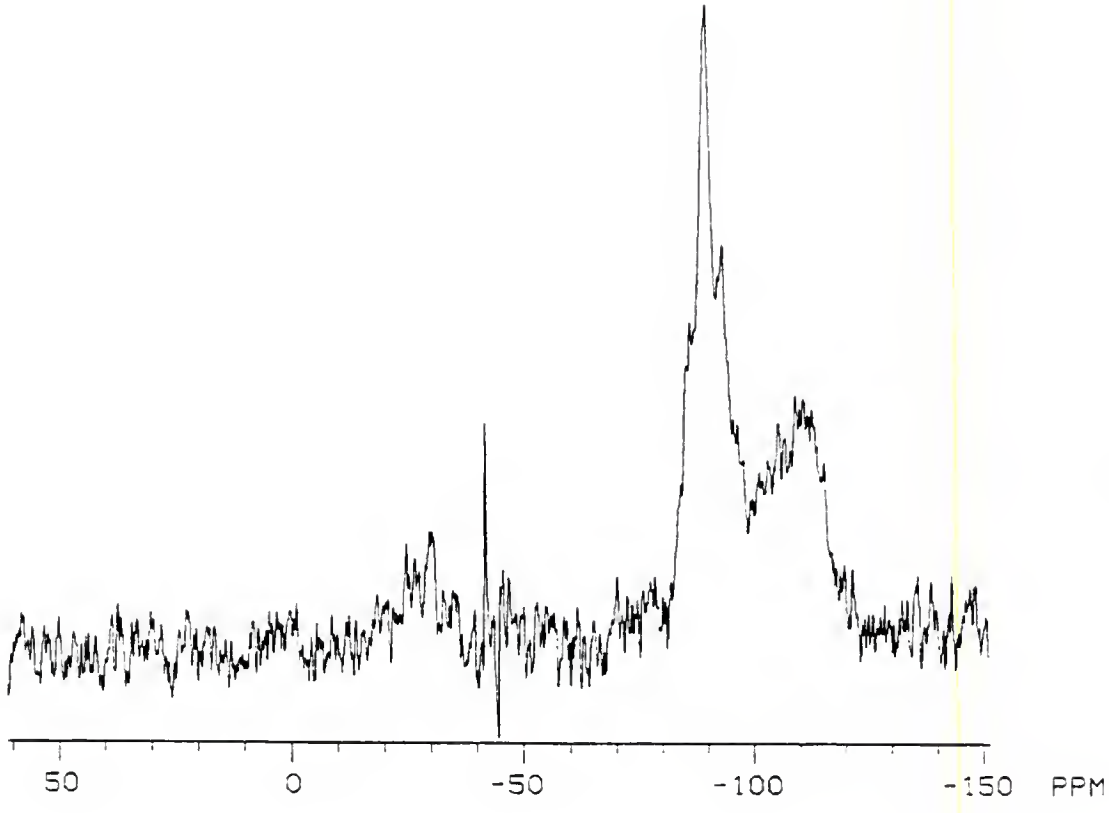


Figure 2-19. A ^{29}Si Solid-State NMR of an $AlCl_2$-SiO_2 Catalyst After Reaction with n-Pentane.

preparation. The following sections will discuss the solid acids use as catalytic cracking and polymerization catalysts.

Characterization of the Radical on the Catalyst Surface

It was reported in the experimental section that when the inorganic oxides treated with aluminum chloride are prepared in refluxing solvents a free-radical species is formed on the solid materials with a g value of 2.012. No hyperfine splitting is observed for the radical signal even at 4 K. In order to identify the radical species present magnetic susceptibility measurements and spin trapping experiments have been conducted on the aluminum chloride treated silicon dioxide made in carbon tetrachloride.

The procedure for the spin trapping experiments using the diamagnetic spin trapping agent DMPO are outlined in the experimental section of this chapter. Whenever the radical was spin trapped in carbon tetrachloride no change in the radical signal was observed indicating that the radical on the surface was not a very reactive species. If the radical is spin trapped in toluene a radical is trapped which has the EPR spectrum shown in Figure 2-20. The signal obtained had a g value of 2.0152 with an observed nitrogen hyperfine splitting constant of 14.225 gauss and a beta hydrogen hyperfine splitting constant of 20.275 gauss. The simulated EPR spectrum shown in Figure 2-21 was obtained using an EPR simulation program as modified by J. Telser.[38-40] When the hyperfine splitting constants obtained from the spectrum in Figure 2-20 are compared to literature values[48,49] of known spin trapped

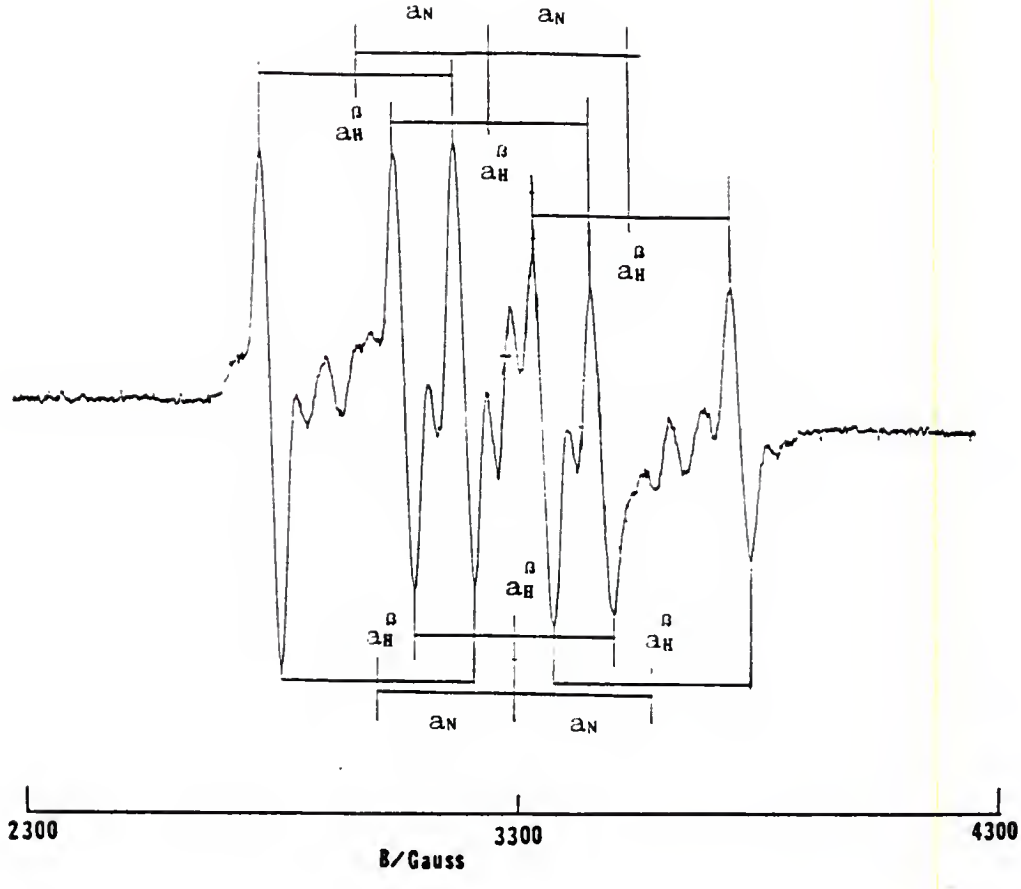


Figure 2-20. Radical on $AlCl_2$-SiO_2 Spin Trapped Using DMPO in Toluene.

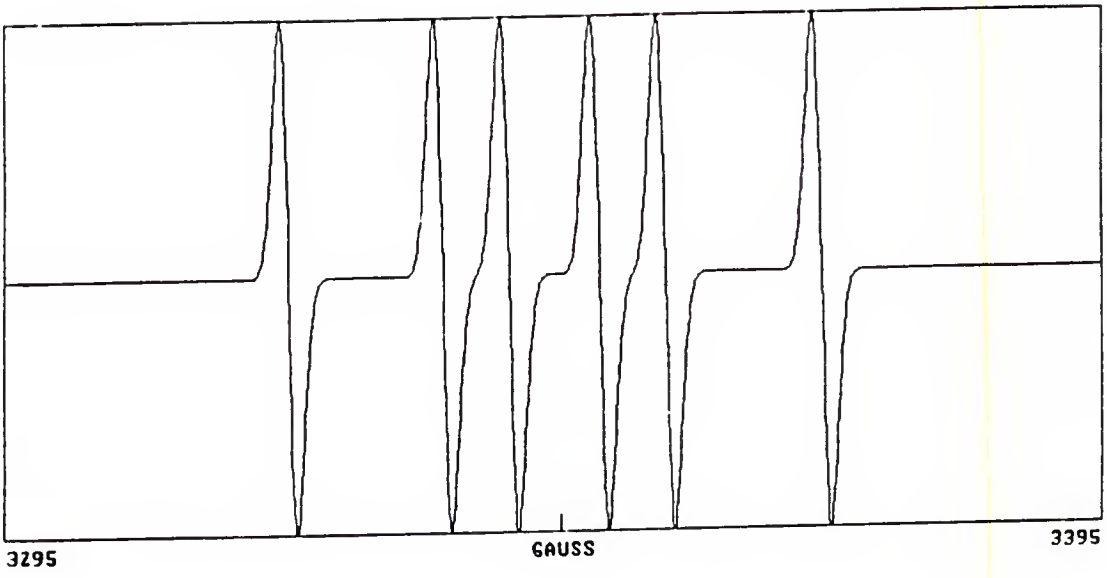


Figure 2-21. EPR Simulation of Radical on $AlCl_2$-SiO_2.

radicals with DMPO, it is found that the EPR spectrum of Figure 2-20 is for the benzyl radical and not the radical on the surface of the catalyst. These results suggest that the radical on the surface is delocalized by the inorganic oxide matrix resulting in a relatively stable free-radical which is not capable of being spin trapped by DMPO.

It has been reported in the literature that compounds such as Al_2Cl_6 act as one-electron oxidizing agents towards electron rich substrates.[43,50,51] A solution of aluminum chloride and dichloromethane is capable of oxidizing any substrate which has a first (adiabatic) ionization energy below 8 eV. The first ionization energies for all the solvents used to prepare the catalyst are well above 8 eV[52] which suggests that the radicals are not derived from the one-electron oxidation of solvent molecules which are then adsorbed onto the catalyst surface. Since the first ionization energies for the elements silicon, aluminum, titanium, magnesium and boron are 8.3 eV[46,52,53] it is reasonable to suggest that the radical is derived from the one-electron oxidation of the support. The radical species generated on the support are delocalized throughout the inorganic oxide matrix causing the radical to be unreactive. Because the EPR spectrum of the radical species on aluminum chloride treated silica gel made in refluxing carbon tetrachloride shows no hyperfine splitting even at 4 K the radical is most likely oxygen based. The inability to spin trap the radical, the absence of any radical chemistry in the cracking of hydrocarbons and the absence of radical initiated polymerizations

all support the idea of delocalized radical species on the catalyst surface. The radical chemistry in the cracking of hydrocarbons and the radical initiated polymerizations will be discussed later in this chapter.

Our catalyst is prepared by the reaction of silica gel with aluminum chloride in a 2:1 ratio by weight. This corresponds to a 4.4:1 mole ratio of silica gel to aluminum chloride. Using this ratio we have calculated a formula weight of 3977.1 grams/mole corresponding to a formula unit of $Si_{44}O_{88}Al_{10}Cl_{20}$. The catalysts sent for magnetic susceptibility measurements[54] were the catalysts prepared in carbon tetrachloride and benzene. For the catalyst made in carbon tetrachloride there were 0.246 unpaired electrons per formula unit and the catalyst made in benzene had 0.289 unpaired electrons per formula unit. A second batch of catalyst made in benzene had 0.142 unpaired electrons per formula unit indicating that the radicals are not very concentrated and that the radical concentration does not change significantly when the catalyst preparation is changed. This also indicates that the radical concentration does not correlate with catalytic activity. The catalyst prepared in carbon tetrachloride is a very active acid cracking catalyst and the catalyst prepared in benzene is about 5 orders of magnitude lower in activity; however, the number of unpaired electrons per formula unit is approximately the same. The radical concentration does not correlate with the catalytic activity of the catalysts.

Titration of Strong Acid Sites with Pyridine

A series of calorimetric titrations in addition to the infrared and NMR studies were performed on several of the solid acid catalysts. The purpose of the titrations was to measure the enthalpy of binding of pyridine to the acid sites present on the catalyst surface. Pyridine was used as the titrant and the procedure was the same as previously described in the literature.[55-57]

The first material titrated was the catalyst prepared by refluxing SiO_2 and Al_2Cl_6 in dry CCl_4 under an N_2 atmosphere. Results from the titrations indicated that the enthalpy of binding of pyridine to the first 13.6% of the surface acid sites ranged from 48.2 Kcal/mole to 17.1 Kcal/mole. The average enthalpy of binding measured for the acid sites titrated was 36.0 Kcal/mole. This value is consistent with the values reported in the literature by other workers for amorphous silica-alumina, aluminosilicates and zeolites.[17,18]

The second material was a catalyst prepared by refluxing a palladium chloride doped silica gel and aluminum chloride in CCl_4 under an N_2 atmosphere. Results from the titrations indicated that the enthalpy of binding from the first 11.8% of the surface sites ranged from 45.0 Kcal/mole to 23.9 Kcal/mole. The average enthalpy of binding measured for the acid sites titrated was 36.5 Kcal/mole. This indicates that the strength of the acid sites on the catalyst are not affected by the addition of a metal chloride. This finding is in agreement with a report in the literature on a palladium

loaded zeolite.[22] Additional work is being conducted on the titration of the solid acids and will be reported in the future.[58]

Catalytic Cracking of Hydrocarbons by a New Solid Acid Catalyst System

The preparation and use of strong acid catalysts and superacids are active areas of research for isomerization, cracking, hydrocracking, dehydration, alkylation, acylation, polymerization, conversion of methanol to gasoline, and so forth.[6] Because of the reported advantages of solid acids,[5] recent research has been focused on the preparation and characterization of stronger solid acids. In view of the higher acidities associated with tetrahedral compared to octahedral aluminum Lewis acids, solid acid catalysts were prepared containing stable tetrahedral aluminum sites. Since one of the largest uses of solid acid catalysts is in the area of catalytic cracking[2,3,59], the solid materials prepared in the experimental section of this chapter were used for various catalytic cracking reactions in both gas-solid flow reactors and liquid-solid batch reactors.

Reaction of a Silica Gel Treated with Aluminum Chloride and Various Straight Chain Hydrocarbons in a Fixed Bed Flow Reactor

The initial experiments for the cracking of hydrocarbons were performed using a fixed bed flow reactor as described in the experimental section of this chapter.

The first reaction conducted was the cracking of n-pentane with an $AlCl_2$-SiO_2 catalyst prepared in CCl_4. Represented in Figure 2-22

is a GC chromatogram of the effluent gas from the reaction of n-pentane, HCl and hydrogen in a 2.5:4:1 ratio by volume with a flow rate of 1 mL/17 sec at 175°C. Products were trapped at -78°C using a Dry Ice-acetone bath and samples were taken using a gas-tight syringe. At this flow rate the ratio of methane, propane, isobutane, n-butane and isopentane to n-pentane is low and corresponds to less than 15% conversion. If the flow rate is slowed by a factor of 2 so that the residence time of the reactants on the catalyst is doubled a marked increase in the percent conversion is observed, Figure 2-23. The increased conversion upon increasing the residence time of the reactants with the catalyst is not unexpected and is a common phenomenon of fixed bed flow reactors. An activity curve for the reaction an $AlCl_2$-SiO_2 catalyst with n-pentane is shown in Figure 2-24. During the progress of the catalytic reaction there is an initial increase in activity which is followed by a decrease in activity of up to three orders in magnitude. After approximately 8 hours the catalyst reaches a near steady-state activity which decreases slowly with time. The activity of the catalyst is similar to other cracking catalysts that are reported in the literature.[2,3] The initial activity can be explained by the presence of a few highly acidic sites on the catalyst which exhibit high activity but rapidly deactivate from coke formation. After the initial surge in activity the less acidic site exhibit a lower activity for cracking and a lower rate of coke formation which causes the activity to remain almost constant with time. The activity of these less acidic sites decrease with time and,

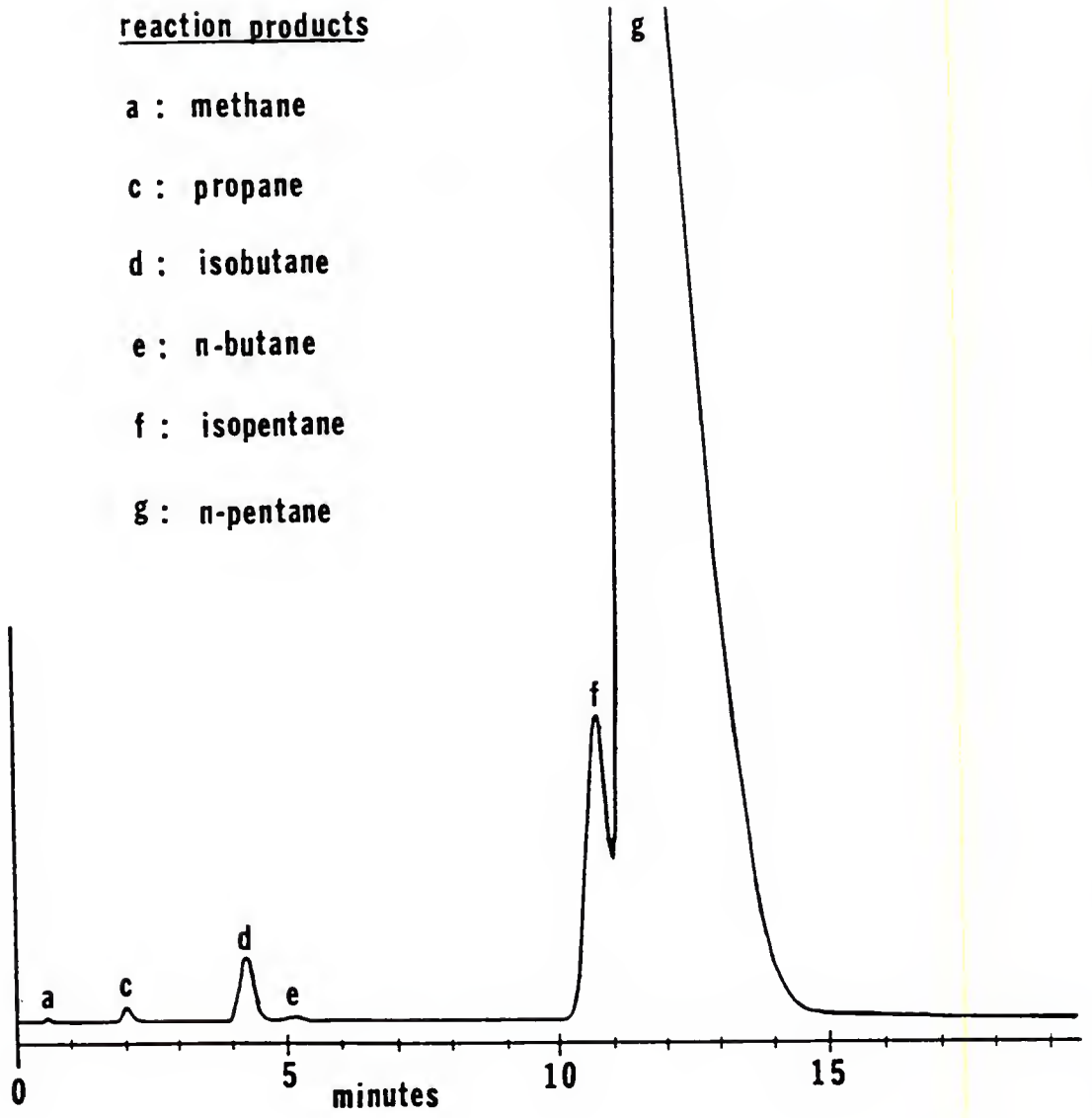


Figure 2-22. GC Chromatogram from the Reaction of n-Pentane with a Solid Acid Catalyst at Fast Flow Rates.

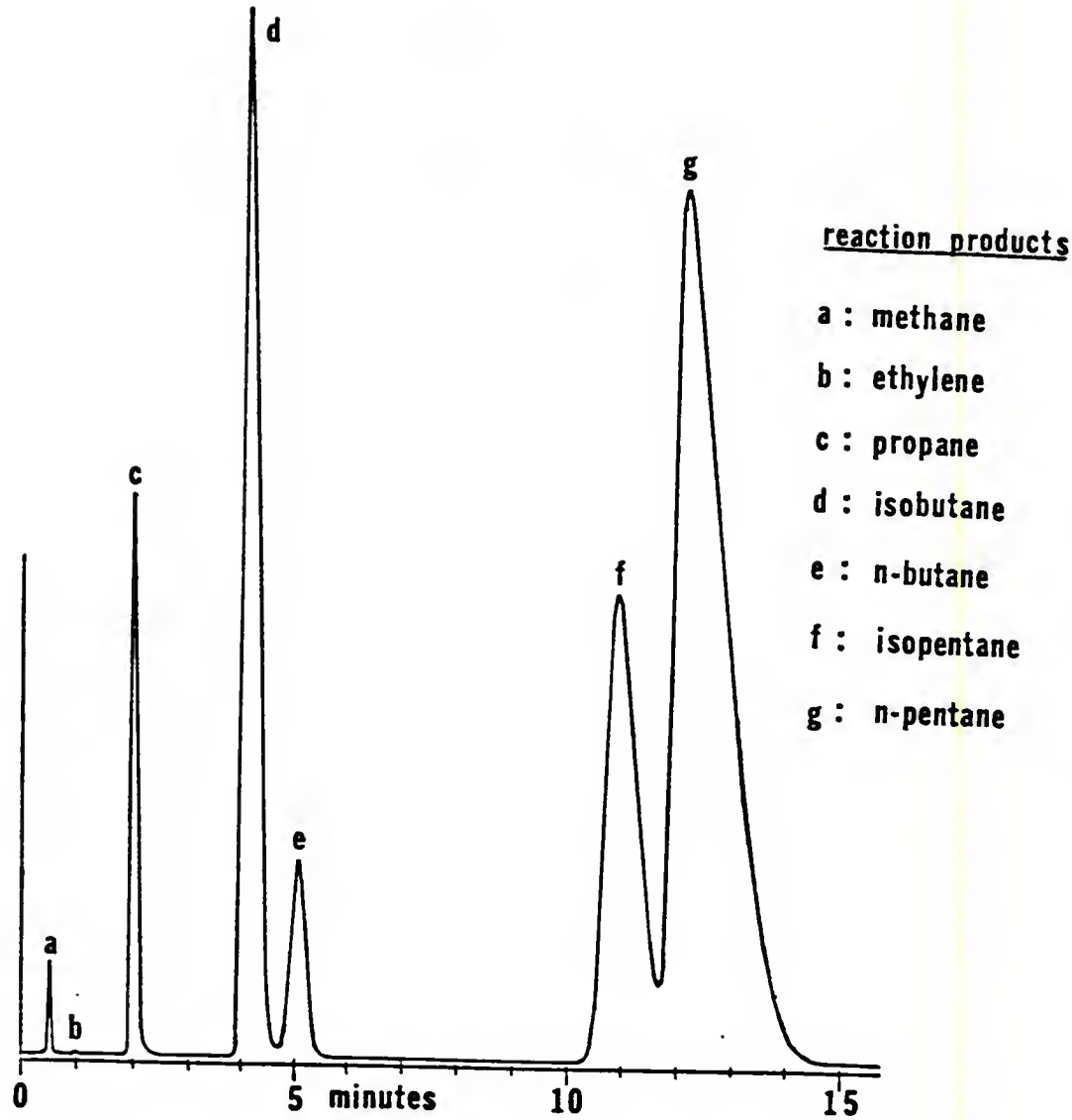


Figure 2-23. GC Chromatogram from the Reaction of n-Pentane with a Solid Acid Catalyst at Slow Flow Rates.

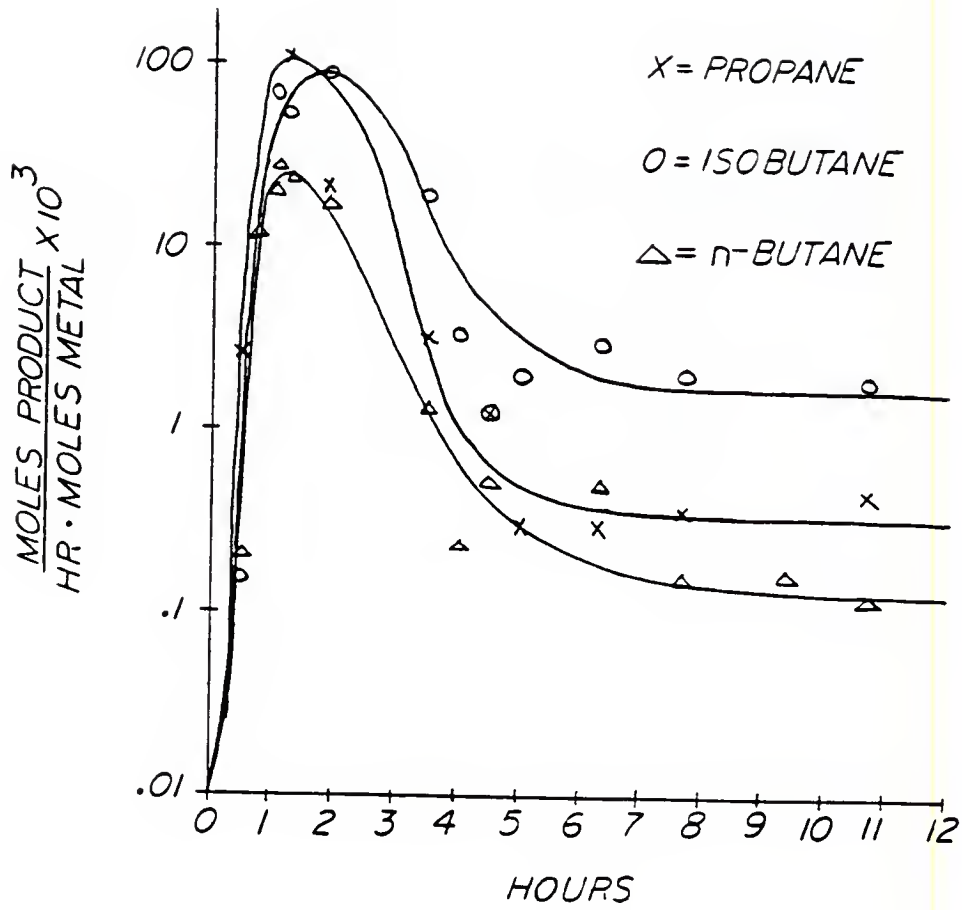


Figure 2-24. Activity Curves for the Reaction of n-Pentane with a Solid Acid Catalyst at 175°C.

after 24 hours with n-pentane as the feed, the catalyst exhibits only minimal activity for cracking.

The activation energy for the cracking of n-pentane is greater than 36.6 Kcal/mole which favors the formation of coke.[2,3] As the chain length of the hydrocarbon is increased, the activation energy required to crack the hydrocarbon decreases with increase in the rate of reaction and decrease in the amount of coke formation. The activation energy for n-heptane is 29.4 Kcal/mole and n-octane has an activation energy of 24.9 Kcal/mole.[3] For hydrocarbons with chain lengths longer than 8 carbons the activation energy does not decrease significantly below that of n-octane.[3]

The next substrate to be used for a cracking reaction was n-heptane. This was to demonstrate that using a longer chain hydrocarbon would increase the activity and the lifetime of the catalyst over what was exhibited for n-pentane. The reaction of n-heptane, HCl and hydrogen in a 1:4:0.1 ratio by volume was conducted at 175°C in a fixed bed flow reactor. Products were collected at -78°C using a Dry Ice-acetone bath and identified by GC and GC/MS. Figure 2-25 represents a GC chromatogram for the cracking of n-heptane by an $AlCl_2$-SiO_2 solid acid catalyst prepared in CCl_4. The mass spectra of the products from the reaction of n-heptane with an $AlCl_2$-SiO_2 solid acid catalyst are shown in Figures 2-26 to 2-30. The major products of this reaction are propane, isobutane and n-butane with minor amounts of n-pentane, isopentane, ethane and methane being produced. In addition to the products listed above, trace quantities of 2-methylhexane were detected by GC/MS as a

product of the reaction and no other products were detected. An activity curve for the cracking of n-heptane by an $AlCl_2$-SiO_2 catalyst prepared in CCl_4 is shown in Figure 2-31. The activity curve for n-heptane is similar to the activity curve for n-pentane and shows that the catalyst exhibits the same catalytic behavior for the two hydrocarbon substrates. The catalyst used in the cracking of n-heptane exhibits an increase in catalyst activity for 10 hours and still shows considerable activity after 90 hours of reaction. The longer time required to reach a near steady-state production of products from n-heptane most likely results from the lower vapor pressure of n-heptane compared to n-pentane which leads to a lower feed rate.

A simplified scheme for the cracking of n-heptane into the major products (propane, isobutane, and n-butane) is shown in Figure 2-32. In this scheme only reactions that proceed to the formation of products are represented. The first step is the abstraction of a hydride ion from the hydrocarbon to form a secondary carbonium ion. The next step is methide and hydride migration to form a more stable tertiary carbonium ion. After a subsequent 2 step hydride migration the isomerized heptane carbonium ion undergoes a ß-scission to form n-butene and the propyl carbonium ion. The propyl carbonium ion can abstract a hydride ion from a substrate molecule to propagate the reaction and form propane which is a major product of the reaction. If the propyl carbonium ion losses a proton, propylene will be formed which in the presence of Bronsted acid

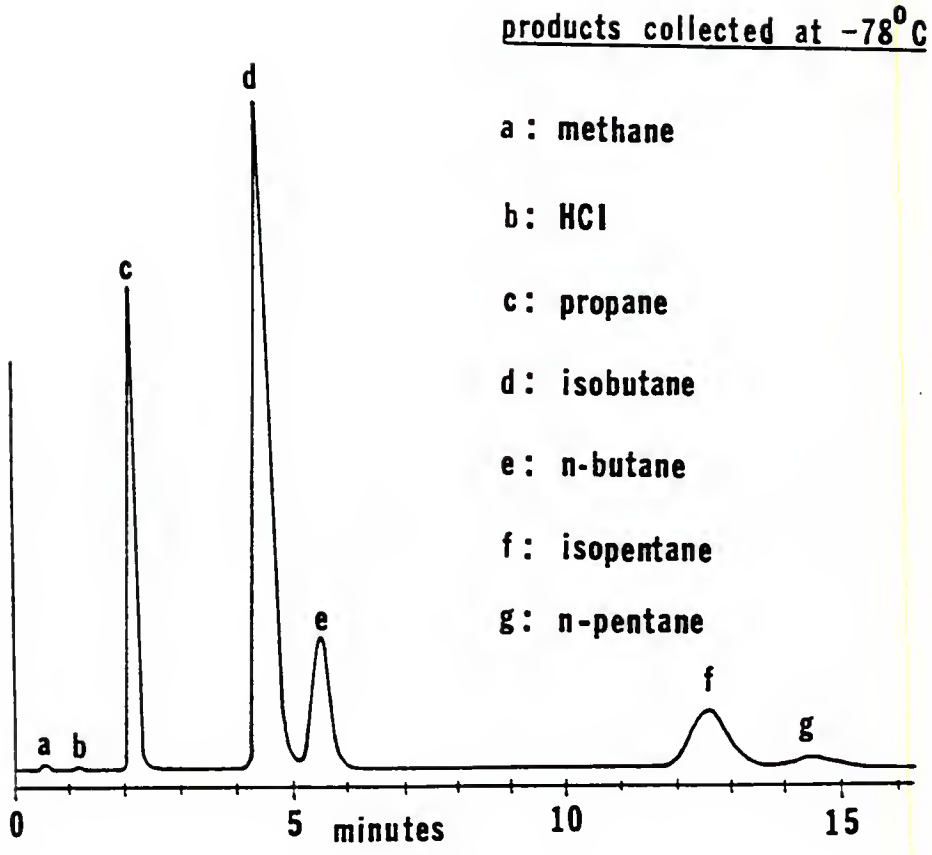
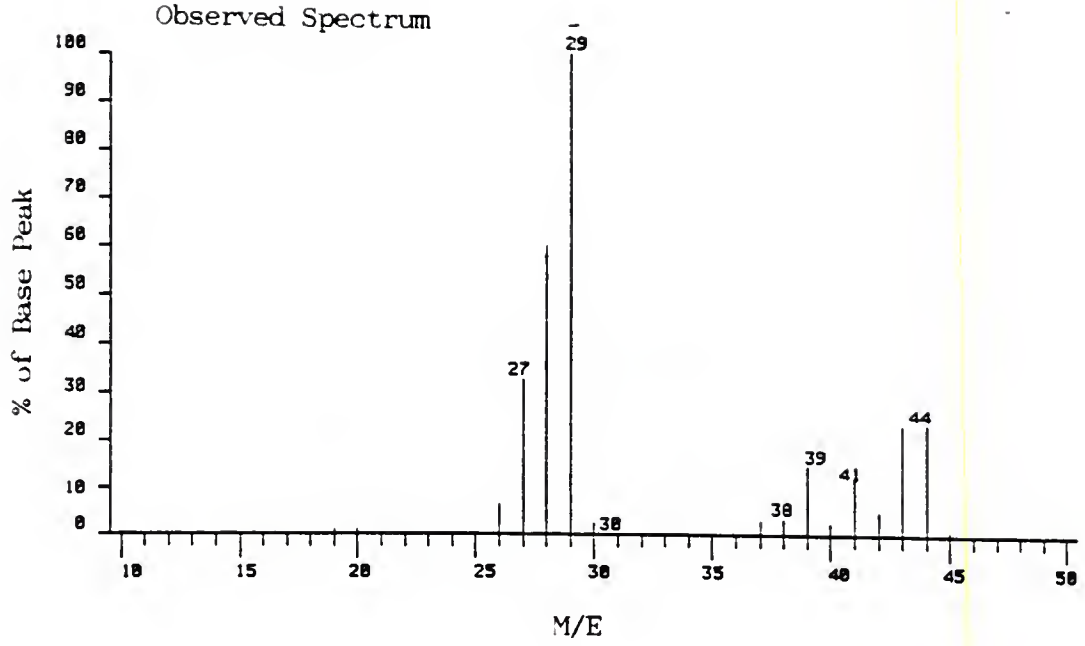


Figure 2-25. GC Chromatogram from the Reaction of n-Heptane with a Solid Acid Catalyst at 175°C.



Reference Spectrum[60]

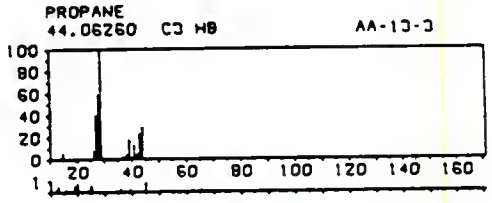
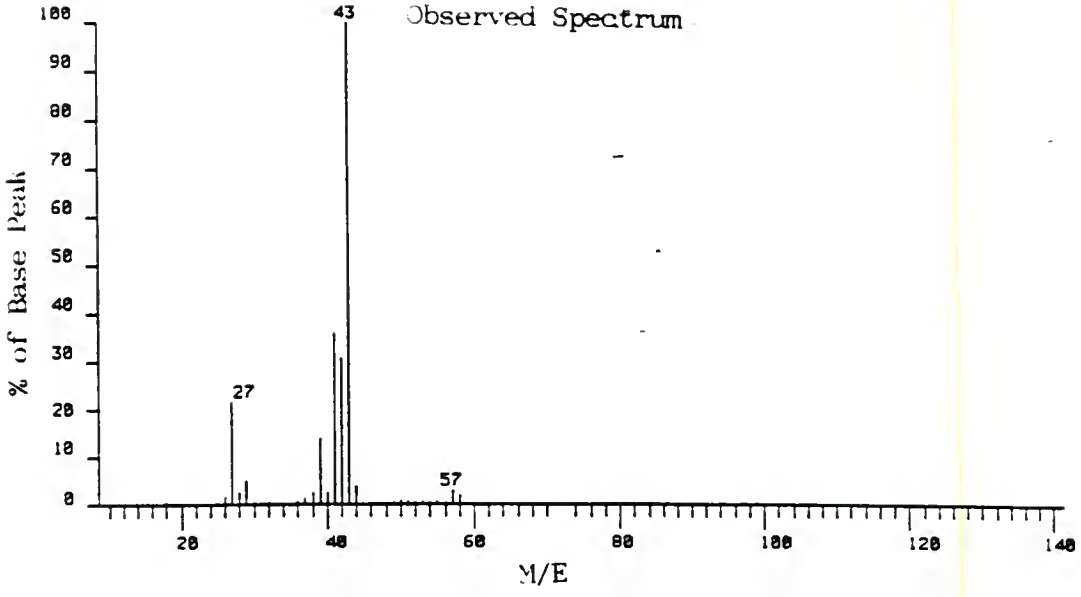


Figure 2-26. Mass Intensity Report for Propane.



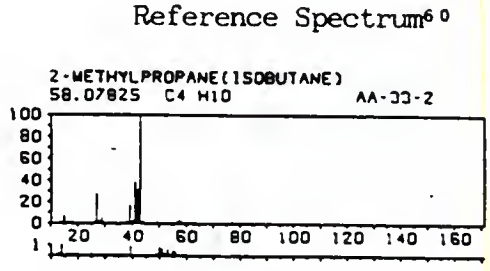
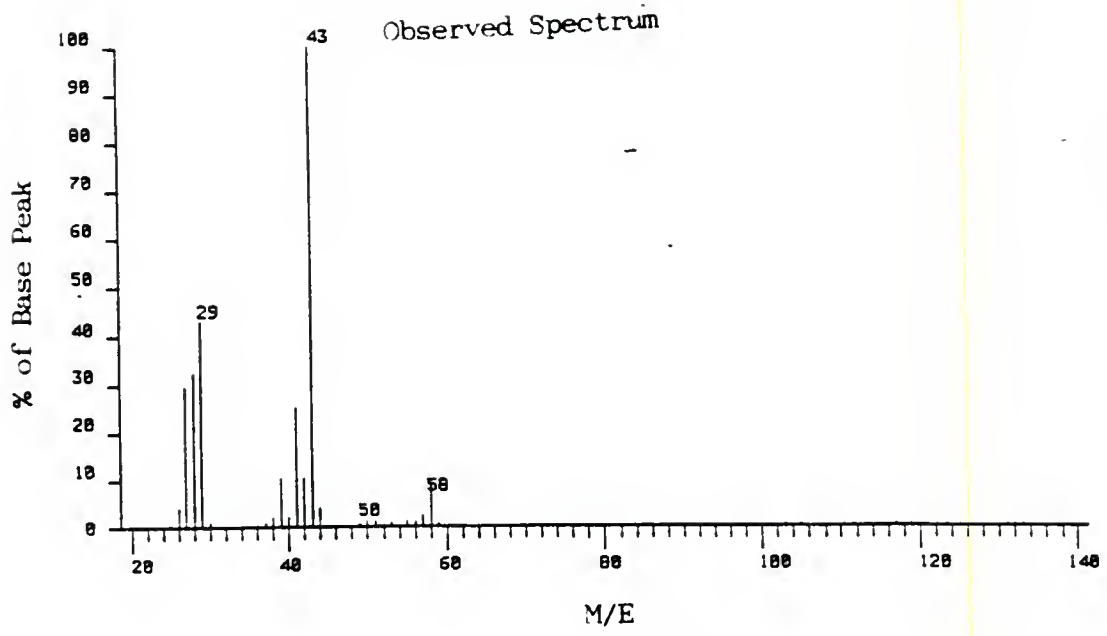


Figure 2-27. Mass Intensity Report for Isobutane.



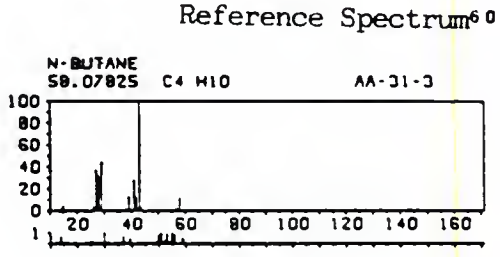
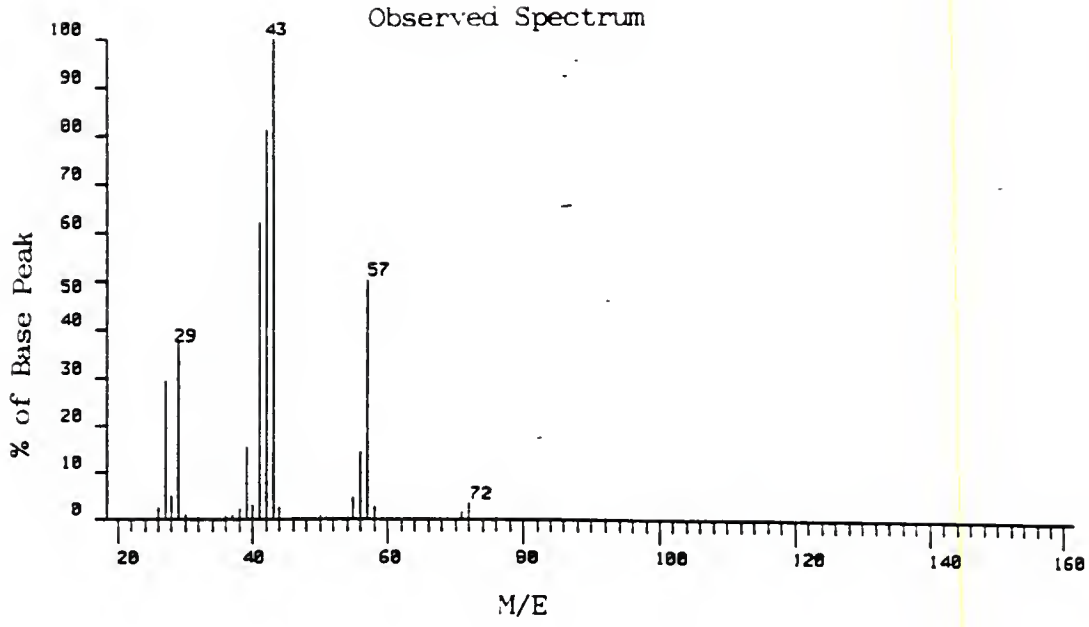


Figure 2-28. Mass Intensity Report for n-Butane.



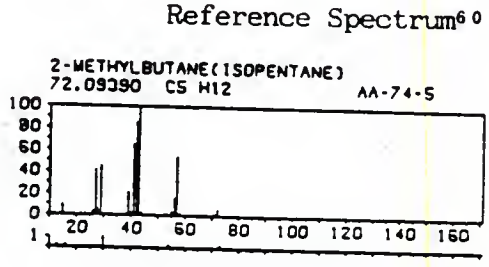
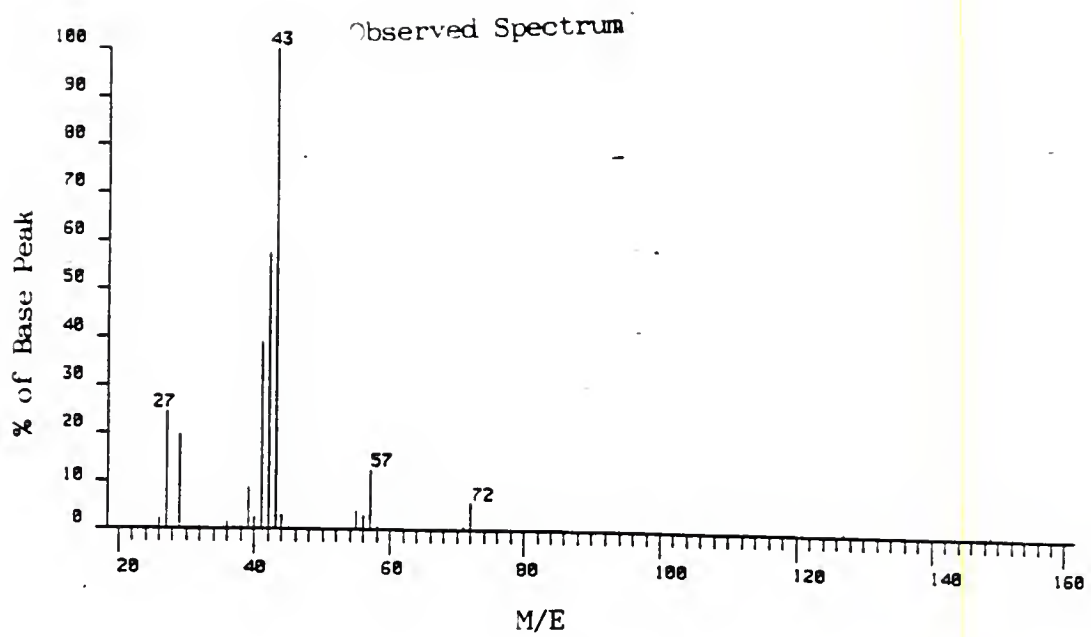


Figure 2-29. Mass Intensity Report for Isopentane.



Reference Spectrum[60]

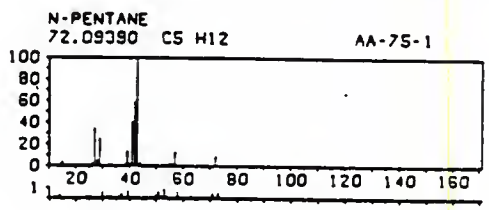


Figure 2-30. Mass Intensity Report for n-Pentane.

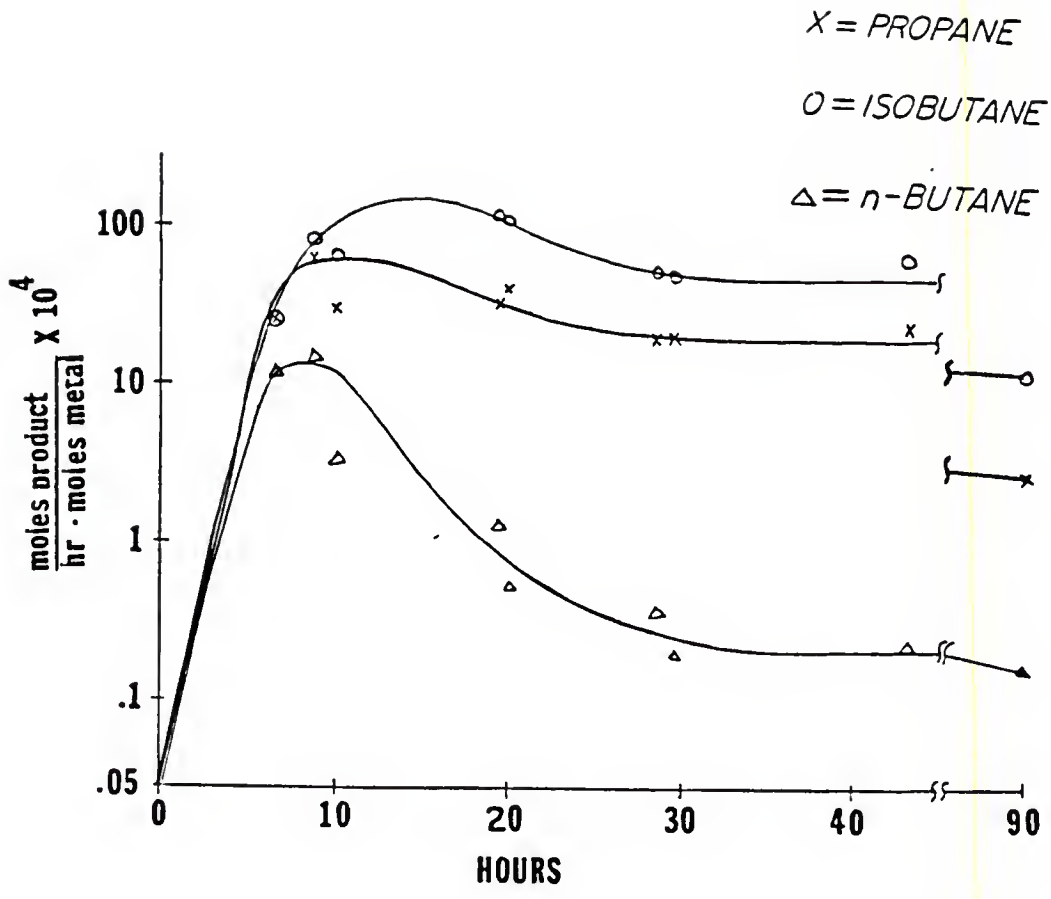
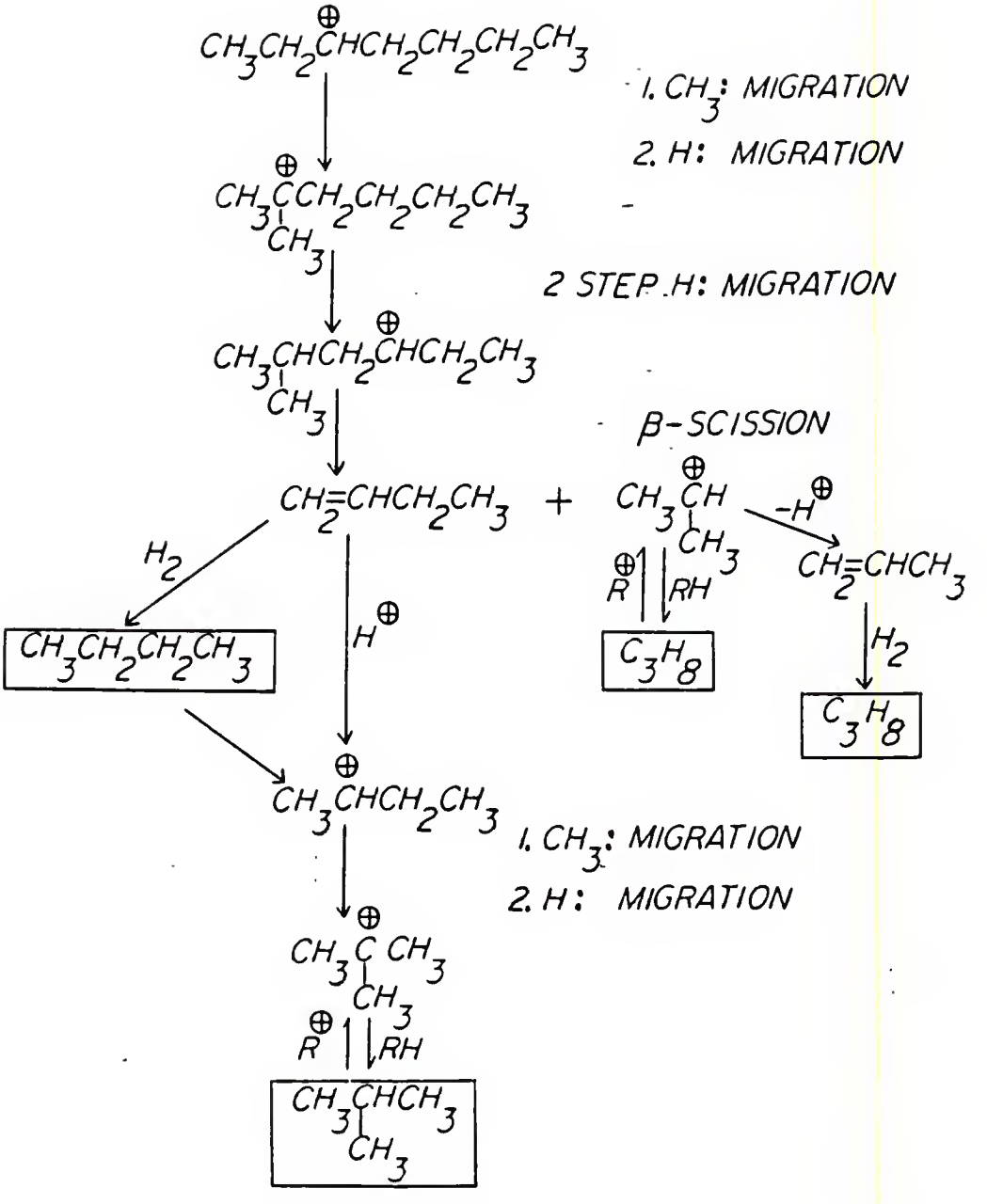


Figure 2-31. Activity Curves for the Reaction of n-Heptane with a Solid Acid Catalyst at 175°C.

Figure 2-32. A Simplified Scheme for the Cracking of n-Heptane.


1. CH3: MIGRATION
2. H: MIGRATION
2 STEP H: MIGRATION
β-SCISSION
1. CH3: MIGRATION
2. H: MIGRATION

sites on the catalyst surface will be reprotonated and reenter the reaction scheme.

The n-butene formed from the ß-scission of the n-heptane carbonium ion could be protonated by a Bronsted acid site to form a secondary butyl carbonium ion. The butyl carbonium ion can then abstract a hydride ion from a substrate molecule to form n-butane which is one of the major products. The secondary butyl carbonium ion may also undergo a methyl and hydride migration to form the isobutyl carbonium ion which will abstract a hydride ion to form isobutane.

All of the reaction steps depicted in the simplified scheme are well documented in the literature and are generally accepted as steps in cracking catalysis. An in depth study of the various reactions that can occur during cracking reactions is outside the scope of this dissertation and detailed reviews of this chemistry may be found in the literature.[2,3,42,44]

Many other reactions may occur simultaneously such as polymerization reactions involving the reaction of olefins with carbonium ions to form high molecular weight hydrocarbons that may be recracked to smaller hydrocarbons. It was indicated in the reaction scheme that hydride abstraction from substrate molecules is a facile reaction. This hydride ion abstraction from hydrocarbon substrate molecules is the source of coke formation which is the leading cause of catalyst deactivation for catalytic reactions involving solid acid catalysts.[2,3] The formation of coke is initiated by adsorption of a hydrocarbon molecule onto the catalyst

surface followed by rapid hydride ion abstraction to form a highly unsaturated hydrocarbon with a low H/C ratio which can no longer desorb from the catalyst surface.[3] This adsorbed hydrocarbon molecule eventually will form a polymeric film that will cover the surface of the catalyst blocking the active centers and deactivating the catalyst.[2]

If the reactions of various hydrocarbons are conducted with carbon tetrachloride as the chlorine source in place of hydrogen chloride the same catalyst selectivity is observed, but when the catalyst exhibits a greater stability and a longer lifetime when carbon tetrachloride is used as the chlorine source. Since the catalyst is prepared in carbon tetrachloride an increase in catalyst stability should result when it is used as a chlorine source. There are several reasons why the use of CCl_4 as a chlorine source may lead to greater catalyst stability. One reason may be that CCl_4 stabilizes the aluminum-chlorine bonds on the catalyst in the same manner described in the catalyst preparation section. Another reason may be that CCl_4 regenerates the catalytically active species which is deactivated when the catalyst abstracts a hydride ion from a hydrocarbon substrate.

When carbon tetrachloride is used as the chlorine source hydrogen chloride and chloroform are detected in the product stream. The amount of chloroform generated in the reaction is of the same order of magnitude as the amount of substrate cracked. With this information a mechanism for the catalytic cracking of hydrocarbons

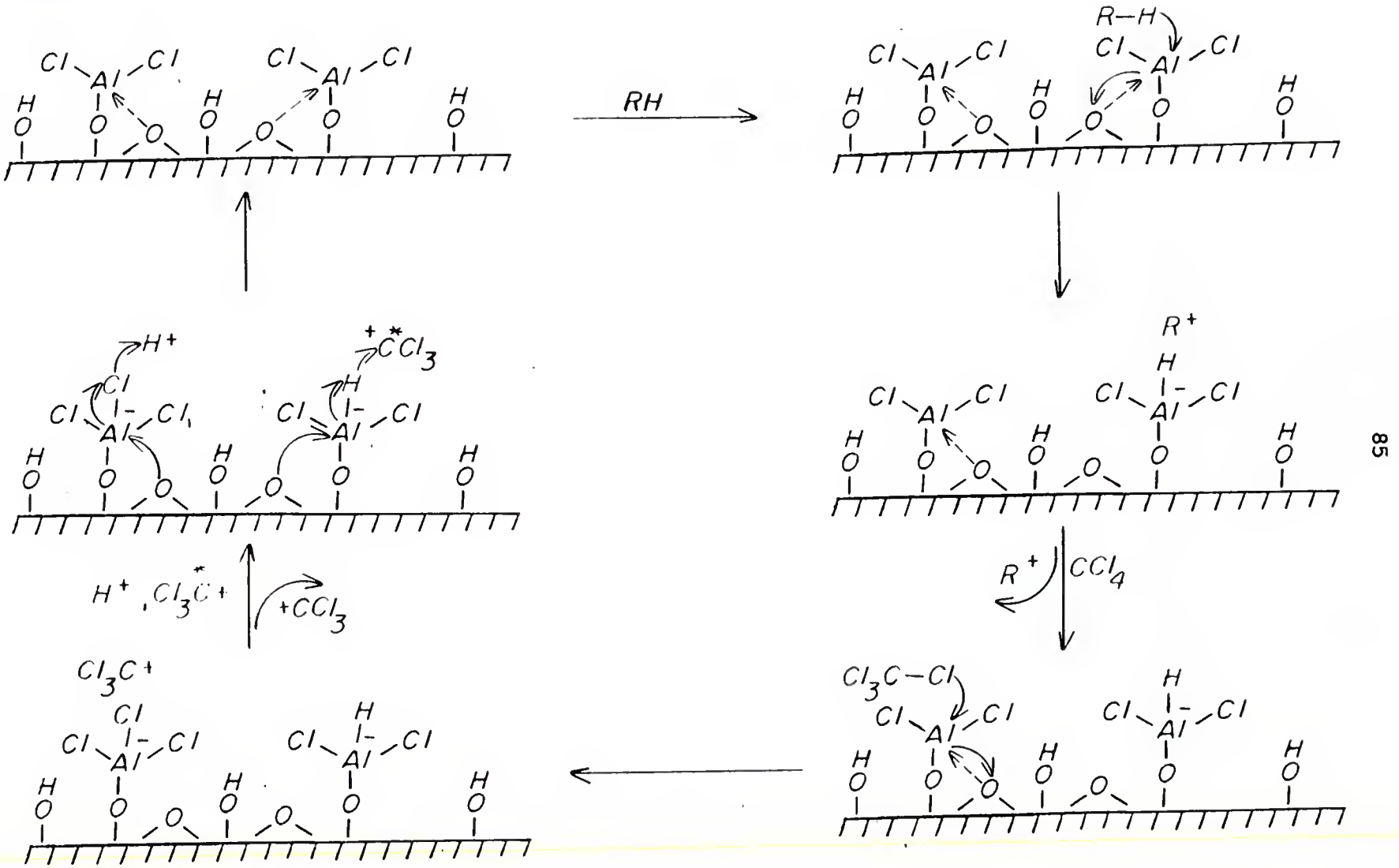
in the presence of CCl_4 can be proposed and is presented in Figure 2-33.

It is generally accepted that the cracking of hydrocarbons proceeds via the generation of carbonium ions through the protonation of alkenes by Bronsted acid or hydride ion abstraction from saturated hydrocarbons with Lewis acids.[2,3] In the mechanism proposed in Figure 2-33 the Bronsted acid sites are not depicted because they are not crucial to the catalytic cycle.

The first step in the reaction would be the abstraction of a hydride ion and the generation of an alkyl carbonium ion. During this reaction the chloroaluminum species would accept the hydride ion and decrease the interaction between the lone pair of the bridging oxygen and the aluminum. The chloroaluminum hydride species formed would have to be regenerated to the starting chloroaluminum species to make the process catalytic.

The process of regenerating the active center could be started by attack of carbon tetrachloride on the chloroaluminum center to generate a species analogous with $Cl_3C^+AlCl_4^-$ which is reported to form upon reaction of aluminum chloride and carbon tetrachloride.[42-44] This species could then dissociate into a Cl_3C^+ carbonium ion and a support-O-$AlCl_3^-$ anion. The Cl_3C^+ carbonium ion then may abstract a hydride ion from a substrate molecule propagating the cracking reaction and forming chloroform which is observed in the productstream. Another path the Cl_3C^+ carbonium ion may take is abstraction of the hydride from the chloroaluminum hydride to reform the active catalytic center.

Figure 2-32. A Simplified Scheme for the Cracking of n-Heptane.


RH
R–H
R+
CCl4
+CCl3

A carbonium ion that has been generated by hydride abstraction may also abstract the hydride from the chloroaluminum center reforming the catalytically active species and a saturated hydrocarbon. The chloroaluminum center which reacted with carbon tetrachloride may be regenerated by reaction with a proton to liberate HCl and form the catalytically active site or stay associated as the HCl adduct to form a Bronsted acid site. The $H^+AlCl_4^-$ species is well documented and at the temperatures employed would dissociate to a great extent to form HCl and the original Lewis acid site.[42,44]

In addition to catalytic cracking, hydrocarbons may undergo thermal cracking. Thermal cracking proceeds by the homolytic cleavage of carbon-carbon and carbon-hydrogen bonds which generate hydrocarbon radicals that react by a radical mechanism.[2] The products generated by thermal cracking are vastly different from the products generated by catalytic cracking. This is a result of the difference in the stability of primary, secondary and tertiary radicals compared to carbonium ions. The relative stability of hydrocarbon radicals are $CH_3\cdot > 1° > 2° > 3°$ and the relative stability of carbonium ions are $3° > 2° > 1° > CH_3^+$.[2,3] For the cracking of n-hexadecane the products characteristic of radical cracking include large amounts of C_1 hydrocarbons, C_2 hydrocarbons are the major products, olefins larger than C_4 are present in the product stream and no branched chain hydrocarbons are present.[2] The products characteristic of carbonium ion type chemistry for the cracking of n-hexadecane are small amounts of C_1 and C_2 hydrocarbons, C_3 to C_6 are the major products, no olefins larger than C_4 are detected in

the product stream and branched chain paraffins are present in the product stream.[2,3]

When the product distribution for the cracking of n-pentane and n-heptane is examined it is found that methane and C_2 hydrocarbons are present in small quantities. The major products are propane, isobutane and n-butane(C_3-C_4 hydrocarbons) with minor amounts of C_5 and higher hydrocarbons present in the product stream. This type of product distribution is consistent with a carbonium ion mechanism and supports the mechanism proposed for the catalytic cracking of hydrocarbons. To further clarify the mechanism for the cracking of hydrocarbons the cracking of isobutane was studied.

The cracking of isobutane has been shown to be a convenient method of determining the mechanism of cracking reactions involving solid acid catalysts.[61,62] Research conducted by McVicker and co-workers demonstrated that isobutane will form different products depending on the method of activation. If isobutane is activated by hydrogen atom abstraction the resulting products will be isobutylene, propylene, methane and hydrogen. If the isobutane is activated by abstraction of a hydride ion the resulting product mixture will be complex and includes isobutylene, n-butane, isomers of butene, propane, propylene, methane, hydrogen and $C_5(+)$ hydrocarbons formed from the reaction of carbonium ions with the olefins in the reaction mixture. The presence of the $C_5(+)$ hydrocarbons is the best indication of a carbonium ion mechanism and is distinctly different from the products formed by a radical mechanism.

When isobutane is reacted with the aluminum chloride treated silicon dioxide catalyst prepared in carbon tetrachloride a complex mixture of hydrocarbons is formed which includes $C_5(+)$ hydrocarbons. A list of the products identified by GC and GC/FTIR are shown in Table 2-2. As seen in Table 2-2 $C_5(+)$ hydrocarbons are formed giving definitive evidence for a carbonium ion mechanism and the catalytic cracking of hydrocarbons.

Some of the other substrates used in the fixed bed flow reactor include n-hexane, dodecane, n-hexadecane, pump oil, activated carbon (charcoal), Pennsylvania soft coal, resid, methanol and dimethyl ether.

The reactions involving the saturated hydrocarbons gave results similar to those obtained for n-pentane and n-heptane. In all cases the major products were C_3-C_4 hydrocarbons with C_1 and C_2 hydrocarbons present in minor amounts. The temperatures employed for the reactions ranged from 110°C to 250°C and catalyst activity increased with increasing temperature.

Methanol and dimethyl ether act as bases toward the acid catalyst and shortened the lifetime of the catalyst considerably. The major product of the methanol and dimethyl ether reactions is methyl chloride which undergoes secondary reactions to form larger chain hydrocarbon and oxygenated products.

Activated carbon and soft coal reacted to give methane, methyl chloride and ethyl chloride which arise from the cracking of methyl and ethyl side chains in the structures of the two materials.

Table 2-2. Products Obtained by Cracking Isobutane.

MAJOR PRODUCTS	MINOR PRODUCTS
Propane	Methane
n-Butane	Ethane
2-Methylbutane	Ethylene
n-Pentane	2,2,4-Trimethylpentane
3-Methylpentane	2,2,3-Trimethylpentane
	2,2,4-trimethylhexane

Lastly, resid when reacted with the solid acid catalyst gave C_1-C_5 aliphatic hydrocarbons and various aromatic compounds. A typical gas chromatograph for the cracking of resid is shown in Figure 2-34. The major products obtained from the reaction include methane, ethylene, methyl chloride, isobutane, ethylchloride, chloropropane, isopentane and benzene. Extensive investigations of these reactions were not conducted due to the complexity of the systems and are reported here only as examples of other substrates that have been used.

Reactions of Various Aluminum Chloride Functionalized Inorganic Oxides with Hydrocarbons in a Batch Reactor

Several disadvantages arise from using the fixed bed flow reactor discussed in the previous section for the conversion of hydrocarbons. The major disadvantage was that constant and steady flow rates could not be obtained using bubblers to introduce gaseous reactants into the system. Quantitative values for the amounts of each reactant had to be based on the number of bubbles entering the system in a given time period. Another disadvantage is that the hydrocarbon reactant had to be introduced by bubbling the reactant gases through the hydrocarbon. In this manner the reactant gases could be saturated with the hydrocarbon vapors and then would be reacted with the catalyst. The amount of hydrocarbon present was dependent on the flow rate of the gases and the vapor pressure ofthe hydrocarbon. For these reasons a quantitative analysis of the system could not be performed and comparison of different catalysts

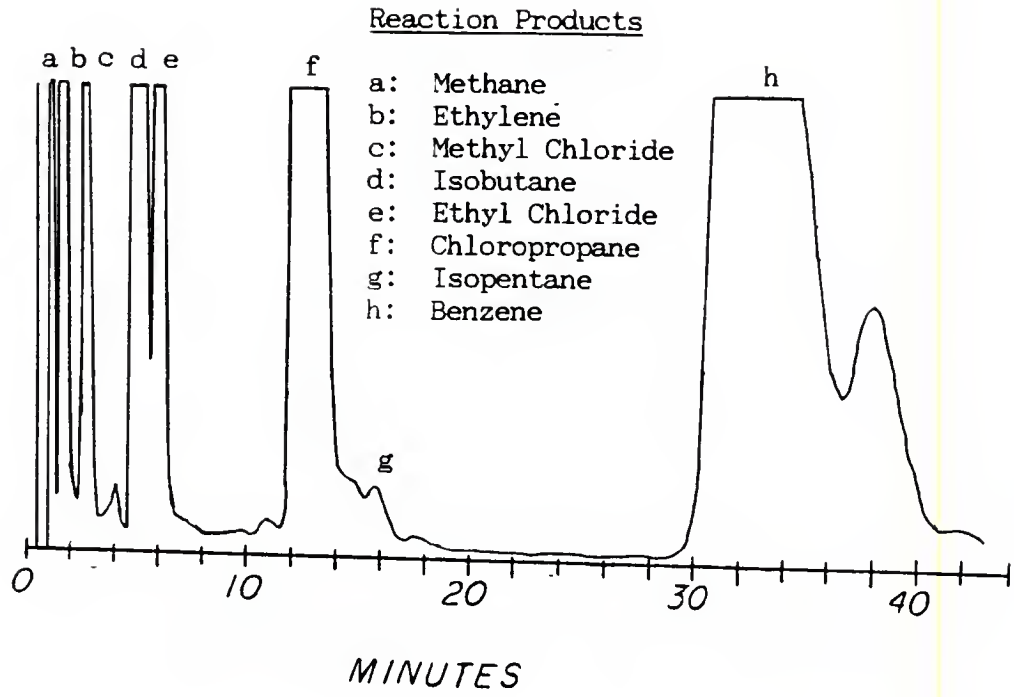


Figure 2-34. GC Chromatogram from the Cracking of Resid with a Solid Acid Catalyst at 175°C.

could not be undertaken because of the variations in reaction conditions. The data obtained from the previous systems should only be used to demonstrate the feasibility of using a catalyst for a particular reaction and a detailed study to compare the activities of various catalysts should be conducted in a more controlled environment.

The batch reactions were conducted in a Parr pressure bottle apparatus, which has been described previously.[36,63] A typical probe molecule used in testing the activities of solid acid catalysts is the cracking of n-hexadecane.[2,3] Since the rates of cracking are affected by the amount of olefin present[23,64] care had to be taken to ensure no olefins were present in the starting hydrocarbon. The n-hexadecane (Aldrich Chemical Company) was 99+% n-hexadecane with the impurities being saturated branched chain isomers. This was confirmed by GC analysis and this source of hydrocarbon has been reported by other workers to be free of any olefin impurities.[64]

The cracking reactions were conducted in a 250 mL batch reactor using 50 mL of a 1.195 M n-hexadecane in carbon tetrachloride solution, 1 to 1.5 grams catalyst and 25 psig H_2 for 18 hours at 100°C. The results for the cracking of n-hexadecane at 100°C by various aluminum chloride functionalized inorganic oxides prepared in carbon tetrachloride are presented in Table 2-3.

The batch reactor is a closed system and previous work[65] has shown that cracking approaches an equilibrium which when conducted in a closed system would hinder the progress of the desired

Table 2-3. Activities for Different $AlCl_2$-Functionalized Supports.

X*	PROPANE**	ISOBUTANE**	n-BUTANE**
SiO_2	4.2 E -3	7.1 E -2	5.4 E -6
Al_2O_3	6.2 E -3	5.3 E -2	3.0 E -6
Silicalite***	1.8 E -2	1.1 E -1	3.3 E -3
B_2O_3	1.1 E -2	5.0 E -2	1.5 E -5
TiO_2	5.0 E -8	5.0 E -4	none
MgO	2.4 E -9	7.8 E -5	none
	BLANKS		
SiO_2	8.0 E -12	5.3 E -10	2.2 E -9
Al_2O_3	none	5.3 E -10	1.0 E -9
Zeolite	none	none	none
TiO_2	none	none	none
B_2O_3	$< 10^{-12}$	8.5 E -10	$< 10^{-10}$
MgO	none	none	none
$AlCl_3$	1.9 E -2	8.9 E -2	1.5 E -4

* MADE IN CCl_4

** UNITS $\frac{\text{MOLES PRODUCT}}{\text{MOLES Al per 18 hrs}}$

*** A high silica zeolite.

reaction. In this case the extent of conversion to light hydrocarbon products was used as a measure of catalyst activity. As the solid acid catalyst strength increases the amount of light end hydrocarbon products should increase. When the solutions and atmosphere of the cracking reactions were analyzed after reaction (GC and GC/FTIR) it was found that the product selectivity for C_5 hydrocarbons was less than that for C_3-C_4 hydrocarbons with no C_6 or higher hydrocarbons detected. Blank supports were prepared by refluxing the support materials in a carbon tetrachloride for 3 days without addition of Al_2Cl_6 and were also investigated under identical conditions. The results for the blank reactions as well as the reaction of free aluminum chloride are shown at the bottom of Table 2-3. The amount of aluminum chloride used was equal to the amount of aluminum chloride used to prepare 1 gram of catalyst. For all untreated supports 1×10^{-9} moles of n-butane, 1×10^{-10} moles of isobutane and 1×10^{-12} moles of propane or less was detected.

The three major products from the cracking of n-hexadecane are propane, isobutane and n-butane. As shown in Table 2-3 the most active catalysts are those prepared on silica gel, a high silica zeolite, boron oxide and alumina. The next most active catalyst after the alumina based catalyst is the catalyst prepared on titanium dioxide. The least active catalyst is the magnesium oxide based catalyst. The observed order in activity is the same as the order in the strengths of the acid catalysts as reflected in the frequency shifts for the Lewis acid band of adsorbed pyridine on the solid acid catalysts. This supports the mechanism for the catalytic

cracking which is based on hydride abstraction from a hydrocarbon molecule. As the Lewis acid strength of the catalyst increases the more favorable the hydride abstraction. As the hydride abstraction capability increases the cracking reaction becomes faster and is reflected in the greater conversion of substrate and the larger percentage of light hydrocarbons formed. In all cases the catalysts are much more active than the untreated supports.

A blank reaction using aluminum chloride led to comparable activity for the three major products but was very unselective leading to large amounts of C_5-C_{15} products and a high molecular weight tar. The aluminum chloride reaction also liberated large quantities of hydrogen chloride gas and is extremely corrosive to the reactor. After one reaction using free aluminum chloride the valves and pressure gauge of the pressure head were corroded to the point that they could not be used again. The reactions using the aluminum chloride functionalized supports have been run in the pressure reactor more than a hundred times with no significant corrosion to the pressure head. The solid acids are much more selective, do not form the high molecular weight tar, are not corrosive to the reactor and no dissolved aluminum chloride is found in the product solution. A typical fluid cracking catalyst (LZ-Y82 zeolite) run under these conditions produces no observable cracking products.

The results for the catalytic cracking of n-hexadecane in carbon tetrachloride using catalysts prepared in different solvents with silicon dioxide as the support are shown in Table 2-4. The

Table 2-4. Activities for $AlCl_2$-SiO_2 Catalysts Prepared in Different Solvents.

SOLVENT*	PROPANE**	ISOBUTANE**	n-BUTANE**
CCl_4	4.2 E-03	7.1 E-02	5.4 E-06
$CHCl_3$	6.0 E-09	4.1 E-05	4.1 E-05
CH_2Cl_2	1.8 E-08	7.1 E-07	3.3 E-07
$ClCH_2CH_2Cl$	2.4 E-08	none	none
C_6H_6	1.0 E-08	none	none

* All reactions run in 50 ml 1.195 M n-hexadecane in CCl_4 @ 100°C and 25 psig H_2.

** UNITS $\frac{\text{MOLES PRODUCT}}{\text{MOLES Al PER 18 HRS}}$

catalyst prepared in carbon tetrachloride is the most active. When the catalyst is prepared in other solvents a significant decrease in the catalyst activity is observed though the catalysts are still more active than the untreated supports. The catalyst activities follow the trend in the frequency shift for the Lewis acid band for pyridine which is consistent with the observations reported for the catalysts prepared on different supports.

Based on the previous results of the previous reactions experiments have been conducted to determine what reaction conditions are needed to optimize the solid acid cracking catalyst. The previous experiments varied the support composition and the solvent used to prepare the catalyst. From these experiments it was determined that the silicon dioxide based catalyst was the most active and that the best solvent to prepare the catalyst was carbon tetrachloride. The next experiments conducted focused on the variation of the weight percent aluminum chloride and the surface area of the support. Experiments were conducted to determine what the effects of pressure, hydrogen and hydrogen chloride had on an active catalyst under reaction conditions.

The amount of aluminum chloride used was 10, 20 and 50 weight percent for the experiments involving variation of catalyst loading. Silicon dioxide was used as the support and was treated identically for each catalyst. The solvent used to prepare each catalyst was CCl_4 and the Al_2Cl_6 solutions were refluxed 2-3 days. All catalysts were run in a Parr pressure reactor at 100°C and 25 psig H_2 in 50 mL of a 1.195 M solution of n-hexadecane in carbon tetrachloride using

1 to 1.5 grams of catalyst. Products were monitored by GC and GC/FTIR. Activities of the catalysts were calculated according to the amounts of propane, isobutane and n-butane produced. Shown in Table 2-5 are the product distributions for the various catalysts and Table 2-6 contains the calculated activities of the catalyst for propane, isobutane and n-butane.

As can be seen in Table 2-5, when decreasing the loading of aluminum chloride from 50 wt% to 20 wt% a slight shift in product distribution occurs and is most pronounced for the C_5 products. A further decrease in the loading from 20 wt% to 10 wt% shows a drastic change in product distribution. The C_1 and C_2 products produced are obtained only in trace amounts. The slight shift in product distribution on changing the loading of aluminum chloride from 50 wt% to 20 wt% may be related to the number and proximity of the acid sites on the catalyst surface as well as the composition of the chloroaluminum species. On a catalyst with a high loading, such as the 50 wt% aluminum chloride catalyst, a substrate molecule may be adsorbed onto several active sites simultaneously which will result in a longer contact time with the catalyst surface and a larger number of small chain products.

When the activities of the 50 wt% and 20 wt% catalysts are compared (Table 2-6) it is seen that the catalyst is two orders of magnitude higher in activity than the 20 wt% catalyst. The activities calculated are corrected for the number of moles of aluminum chloride present so the activities would be the same if

Table 2-5. Product Distribution for Catalysts with Varying Percents of Aluminum Chloride on Silicon Dioxide.

PRODUCT	SiO_2 % PRODUCT*	10 wt% CATALYST % PRODUCT*	20 wt% CATALYST % PRODUCT*	50 wt% CATALYST % PRODUCT*
METHANE	61.849	87.460	0.808	0.518
ETHYLENE	none	5.540	0.147	0.056
ETHANE	21.829	none	none	0.010
HCl	none	7.000	0.134	none
PROPANE	0.099	none	2.446	6.655
MeCl	7.471	none	none	none
ISOBUTANE	2.259	none	70.283	75.466
n-BUTANE	6.493	none	none	1.444
ISOPENTANE	none	none	26.182	15.851

* % Product as represented by integrated areas of product peaks using an integrating recorder.

Table 2-6. Activities for Catalysts with Varying Percents of Aluminum Chloride on Silicon Dioxide.

PRODUCT	10 wt% CATALYST MOLES PRODUCT* / MOLES Al	20 wt% CATALYST MOLES PRODUCT* / MOLES Al	50 wt% CATALYST MOLES PRODUCT** / MOLES Al
PROPANE	none	2.19 E-05	1.64 E-02
ISOBUTANE	none	1.50 E-03	1.62 E-01
n-BUTANE	none	none	7.98 E-05

* At the end of 18 hours.

** At the end of 14 hours.

there was a first order dependence on the amount of aluminum chloride present. Since there is a 100 fold increase in activity on proceeding from a 20 wt% loading to a 50 wt% loading other factors must be involved. These observations suggest the need for more than one acid site for catalysis and that the active sites are $-O-AlCl_2$ species and not just any chloroaluminum species. A significant number of $-O-AlCl_2$ groups bonded to the surface hydroxyl groups of the silicon dioxide would only be formed at the higher loadings. The catalyst made using a 10 wt% loading of aluminum chloride showed no activity for cracking and gave only trace amounts of methane, ethylene and HCl. The activity of the 10 wt% catalyst is less than the blank reaction which involved dried silicon dioxide that was refluxed in CCl_4 and run under identical conditions.

Experiments on the variation of surface area involved the use of silicon dioxide from AESAR of 215 m^2/gram and 690 m^2/gram surface area and our original silicon dioxide from Davison Chemical (Grade 62) which has a surface area of 320 m^2/gram. Catalysts were prepared using 50 wt% aluminum chloride and run under reaction conditions identical to those for the experiments on the variation of catalyst loadings. Product distributions and catalyst activities for the 215 m^2/gram and 690 m^2/gram catalysts are given in Tables 2-7 and 2-8 respectively.

The product distributions for each catalyst are very similar and the activity of the 215 m^2/gram catalyst is roughly one order of magnitude more active than the 690 m^2/gram catalyst. When comparing the catalysts made using the silicon dioxide from AESAR and the

Table 2-7. Product Distribution for Catalysts with Varying Surface Areas Using 50 wt% Aluminum Chloride on Silicon Dioxide.

PRODUCT	215 m^2/gram CATALYST % PRODUCT*	690 m^2/gram CATALYST % PRODUCT*
METHANE	0.110	3.574
ETHYLENE	0.054	0.063
HCl	0.009	0.093
PROPANE	0.710	2.512
METHYLCHLORIDE	none	0.176
ISOBUTANE	73.463	71.222
ISOPENTANE	25.654	22.054
n-PENTANE	none	0.306

* % Product as represented by integrated areas of product peaks using an integrating recorder.

Table 2-8. Activities for Catalysts with Varying Surface Areas Using 50 wt% Aluminum Chloride on Silicon Dioxide.

PRODUCT	215 m^2/gram CATALYST % PRODUCT*	690 m^2/gram CATALYST % PRODUCT*
PROPANE	7.68 E-06	1.82 E-06
ISOBUTANE	1.46 E-03	1.49 E-04

* At the end of 18 hours.

catalyst using Davison silicon dioxide there is a significant difference in the catalyst activities. This difference in activity may be due to the manner in which the supports are manufactured or the way in which the catalysts were prepared. The catalyst selectivities are similar for each of the catalysts and are indicative of a carbonium ion cracking mechanism. What has been determined is that a 50 wt% loading on a 340 m^2/gram silicon dioxide results in the most active catalyst and the coverage of aluminum chloride on the catalyst surface is approximately 80% based on the number of available surface hydroxyl groups.

One of the results from the first set of experiments is that the catalyst prepared from the silicon dioxide with a loading of 50 wt% aluminum chloride is the most active for cracking. The 50 wt% catalyst has been prepared using a variety of supports such as silicon dioxide, aluminum oxide, boron oxide, titanium dioxide, magnesium oxide and an all-silica zeolite. Of the supports mentioned the all silica zeolite, silicon dioxide and aluminum oxide prepared catalysts are the most active for catalytic cracking. As a result the next set of experiments which involve the dependence of pressure, hydrogen gas and hydrogen chloride on catalytic activity used the silicon dioxide catalyst.

The first experiment was conducted at 100°C using the 50 wt% catalyst, 50 mL of a 1.195 M n-hexadecane in carbon tetrachloride solution under atmospheric pressure of hydrogen gas. The next experiment was conducted under identical conditions except that the reaction was carried out under a helium atmosphere at 25 psig. The

third experiment was carried out with the helium at atmospheric pressure and the last experiment was performed using 25 psig hydrogen chloride gas. Product distributions and catalyst activities are shown in Tables 2-9 and 2-10 respectively. From these experiments it can be concluded that the presence of hydrogen in the reaction system slightly enhances catalyst activity. The catalyst is slightly sensitive to the reaction system pressure and hydrogen chloride may be used in the place of hydrogen gas. The catalysts used in the previous reactions have been used for several cracking cycles and still show catalytic activity after 117 hours under reaction conditions.

In continuing work on cracking of n-hexadecane, the reactions were run at higher temperatures. In order to ensure that our catalyst would still be in a liquid phase a new solvent was chosen to run the reaction. Tables 2-11 and 2-12 show the results of the experiments in tetrachloroethylene (perc) compared to the reactions done in CCl_4. Table 2-11 gives the activities of the SiO_2 based catalyst in CCl_4 and perc. For the reactions in CCl_4 there is no corresponding increase in the activity of the catalyst as the temperature is increased. In contrast, the reactions carried out in perc show an increase in activity as the temperature is increased. As seen in Table 2-12, the product distribution changes upon switching from CCl_4 to perc. The large amount of ethylene present comes from the ethanol present in the perc as a stabilizer (0.75%). The ethanol would have less of an effect on the percentage of other products.

Table 2-9. Product Distribution for the 50 wt% Aluminum Chloride on Silicon Dioxide Under Various Experimental Conditions.

PRODUCTS	25 PSIG H_2 % PRODUCT[1]	0 PSIG H_2 % PRODUCT[1]	25 PSIG He % PRODUCT[1]	0 PSIG He % PRODUCT[1]	25 PSIG HCl % PRODUCT[1]
METHANE	0.518	0.073	0.199	0.252	0.177
ETHYLENE	0.056	0.006	0.016	none	none
ETHANE	0.010	none	none	none	none
HCl	none	none	0.014	none	none
PROPANE	6.655	2.440	4.185	3.034	3.552
MeCl	none	0.008	none	none	none
ISOBUTANE	75.466	73.299	70.843	72.788	75.872
n-BUTANE	1.444	0.866	1.333	0.644	0.976
ISOPENTANE	15.851	23.308	23.158	23.303	19.407
n-PENTANE	none	none	0.252	none	0.015

[1] % PRODUCT AS REPRESENTED BY INTEGRATED AREAS OF PRODUCT PEAKS USING AN INTEGRATING RECORDER

Table 2-10. Activities for the Catalyst with 50 wt% Aluminum Chloride on Silicon Dioxide under Various Experimental Conditions.

	25 PSIG H_2	0 PSIG H_2	25 PSIG He	0 PSIG He	25 PSIG HCl
PRODUCT	MOLES PRODUCT[1] / MOLES Al	MOLES PRODUCT[2] / MOLES Al	MOLES PRODUCT[3] / MOLES Al	MOLES PRODUCT[2] / MOLES Al	MOLES PRODUCT[3] / MOLES Al
PROPANE	1.64 E-02	2.03 E-03	4.68 E-03	1.44 E-03	5.42 E-03
ISOBUTANE	1.62 E-01	5.99 E-02	7.01 E-02	3.35 E-02	1.05 E-01
n-BUTANE	7.98 E-05	6.30 E-06	2.76 E-05	5.72 E-06	2.99 E-05

[1] At the end of 14 hours.

[2] At the end of 20 hours.

[3] At the end of 18 hours.

Table 2-11. Activities for $AlCl_2$-SiO_2 Catalyst in Different Solvents and Different Temperatures.

SOLVENT	TEMPERATURE	MOLES PROPANE / MOLES Al	MOLES ISOBUTANE / MOLES Al	MOLES n-BUTANE / MOLES Al	HOURS
CCl_4[1]	100C	1.64 E-2	1.62 E-1	8.03 E-5	14
CCl_4[2]	150C	6.54 E-3	8.24 E-2	2.64 E-3	8
PERC[3]	100C	7.71 E-4	1.46 E-4	1.97 E-3	12
PERC[3]	150C	8.24 E-4	1.46 E-2	1.00 E-2	12
PERC[3]	200C	9.06 E-3	4.02 E-2	8.58 E-3	12

1 50 ml of a 1.195M n-hexadecane in CCl_4 solution.

2 25 ml CCl_4, 75 ml n-hexadecane.

3 50 ml PERC, 25 ml n-hexadecane.

Table 2-12. Product Distributions for $AlCl_2$-SiO_2 Catalyst in Different Solvents and Different Temperatures.

PRODUCT	100°C*	150°C*	100°C*	150°C**	200°C**
METHANE	0.518	3.020	0.614	2.017	3.103
ETHYLENE	0.056	0.096	9.159	2.779	10.487
ETHANE	0.010	1.095			
PROPANE	6.655	4.561	6.269	2.361	9.277
ISOBUTANE	75.466	66.298	28.676	46.453	51.516
n-BUTANE	1.444	0.076	58.832	33.328	15.179
ISOPENTANE	15.851	24.854	2.092	13.063	10.438

* Reaction conducted in CCl_4.

** Reaction conducted in Tetrachloroethylene (Perc).

The difference in activity for the two solvents at various temperatures is related to the basicity of the solvents and the activation energies for cleavage of the carbon-chlorine bonds. Tetrachloroethylene is a more basic solvent than carbon tetrachloride and coordinates to the catalysts acid sites without dissociation. At 100°C there is enough thermal energy in the system to dissociate the carbon tetrachloride-catalyst complex but there is still a substantial interaction between tetrachloroethylene and the acid catalyst. The tetrachloroethylene adsorbed on the catalyst surface blocks substrate molecules from reaching reactive sites. When the temperature is increased to 200°C the thermal energy of the reaction system is great enough to substantially dissociate the tetrachloroethylene-acid site interaction and raise the catalytic activity to the same level as carbon tetrachloride at 100°C. The net effect is to decrease the interaction between the acid and solvent which would lead to a greater interaction between the acid sites and the hydrocarbon substrate.

Another effect which adversely effects the catalyst activity is the increase in vapor pressure of the solvents as the temperature increases. The vapor pressure of carbon tetrachloride at 150°C is slightly over 5 atmospheres[52] which would tend to shift the products toward larger chain products as indicated in Table 2-12.

In addition to running reactions in perc it was desireable to know what the heaviest feed percentage was for our catalyst system. Tables 2-13 and 2-14 summarized the results from cracking experiments using 35%, 90%, and 95% n-hexadecane in the feed. The

Table 2-13. Activities for $AlCl_2$-SiO_2 Catalyst at Different Feed Percents in Carbon Tetrachloride at 100°C and 25 psig H_2.

PRODUCT	35% HEXADECANE	90% HEXADECANE	95% HEXADECANE
PROPANE	1.64 E-2	5.40 E-3	3.59 E-3
ISOBUTANE	1.62 E-1	1.42 E-2	1.23 E-1
n-BUTANE	7.98 E-5	3.44 E-5	1.20 E-5
	14 HRS	18 HRS	8 HRS

Table 2-14. Product Distributions for $AlCl_2$-SiO_2 Catalyst at Different Feed Percents in Carbon Tetrachloride at 100°C and 25 psig H_2.

PRODUCT	35% HEXADECANE	90% HEXADECANE	95% HEXADECANE
METHANE	0.518	0.019	0.061
ETHYLENE	0.056	0.004	0.002
ETHANE	0.010	none	none
PROPANE	6.655	2.455	2.004
ISOBUTANE	75.466	69.247	71.675
n-BUTANE	1.444	0.766	0.504
ISOPENTANE	15.851	27.434	25.753
n-PENTANE	none	0.075	none

activity of the catalyst for C_1-C_4 is lowered slightly upon increasing the amount of substrate and there is a corresponding shift to larger chain products. This is what one would expect as the feed percent is increased. The larger hydrocarbons (C_9-C_{16}) are much easier to activate for cracking than light hydrocarbons (C_1-C_6) and will react faster. The concentration of heavy hydrocarbons must be depleted before significant cracking of the lighter hydrocarbons products will occur. Also with a high concentration of hydrocarbon, it takes much longer for the CCl_4 to regenerate an active site because it must compete with the large hydrocarbons chemisorbed and physisorbed on the catalyst surface.

This is substantiated by the fact that the CCl_4 used in the reaction is converted to $CHCl_3$ and CH_2Cl_2 during the course of the reaction. It also appears that the CCl_4 is used up on the same scale as the hexadecane is converted to products. If the reaction is run in perc 1,1,2-trichloroethane is detected which suggests the replacement of a carbon-chlorine bond by a carbon-hydrogen bond followed by hydrogenation of the double bond. This is consistent with the proposed mechanism for the solid acid catalyst system.

Reactions of Hydrocarbon Substrates with an Improved Solid Acid Catalyst in a Syringe Pump Flow Reactor

It has been learned from the previous experiments involving hydrocarbon substrates that the 50 wt% aluminum chloride on silica gel catalyst is one of the most active cracking catalysts. For reactions involving the $AlCl_2$-SiO_2 catalyst it is known that a chlorine source is needed to maintain catalytic activity and that

carbon tetrachloride is the best chlorine source. The effect of pressure has an inverse effect on catalyst activity and the use of hydrogen gas results in only a slight increase in catalyst activity. Though the use of carbon tetrachloride extends the lifetime of the catalyst, the catalyst eventually deactivates (the activity decreases to a very low level) due to the formation of coke. This coke formation results from the hydride abstraction from substrate molecules by carbonium ions. Since the catalyst shows only a slight increase in activity when hydrogen gas is used and saturated products are formed as products during the cracking reaction, the hydrogen used to form the cracking products must come from substrate molecules.

Because there is an apparent need for hydride ions in the reaction system, a noble metal was placed on the catalyst surface to activate molecular hydrogen in order to supply the needed hydride ions. This would increase the availability of hydride ion, cause an increase in activity and a decrease in coke formation. The use of noble metals on solid acid catalysts is not new and solid acid catalysts that are made with noble metals are used in areas such as hydrocracking, reforming and other hydro processes.[1,2,3,59]

Using a syringe pumped flow reactor which was described in the experimental section, two reactions were conducted in which n-hexadecane was cracked by an $AlCl_2$-SiO_2 catalyst and a $Pd(II)Cl_2AlCl_2$-SiO_2 catalyst at 175°C. The carbon tetrachloride and n-hexadecane were delivered by a syringe pump into the reactor in a preheater zone. The preheater zone consisted of a packed tube of

1/16 inch glass spheres which were the same temperature as the catalyst zone and was ten times the catalyst bed length. In the preheater zone the liquid reactants were vaporized and mixed with a hydrogen carrier gas. This reaction mixture was heated to reaction temperature and then passed through the catalyst.

The reaction system consisted of a motorized syringe containing 4.5 ml of a 75% by volume n-hexadecane in carbon tetrachloride and equipped with a teflon delivery tube. The teflon delivery tube enters the glass reactor through a septum and ends just before the catalyst zone. Hydrogen is used as the carrier gas and the flow of the gas is downward against a glass frit which supports the catalyst zone. Both n-hexadecane reactions were carried out at 175°C. The $AlCl_2$-SilicaGel catalyst worked very well and showed higher activity in the syringe pumped reactor than any other reactor previously used. Product distribution and catalyst selectivity were similar to previous experiments using a glass flow system. The product distribution and catalyst activity for the $AlCl_2$-SilicaGel catalyst are shown in Figure 2-35. Some chloroform was observed and in an amount that would indicate a near 1:1 ratio between the amount of n-hexadecane converted and the amount of carbon tetrachloride consumed. Large quantities of carbon tetrachloride were detected in the product stream reconfirming this result.

The $Pd(II)Cl_2AlCl_2$-SilicaGel catalyst was extremely active for the catalytic cracking of n-hexadecane at 175°C. Extremely large

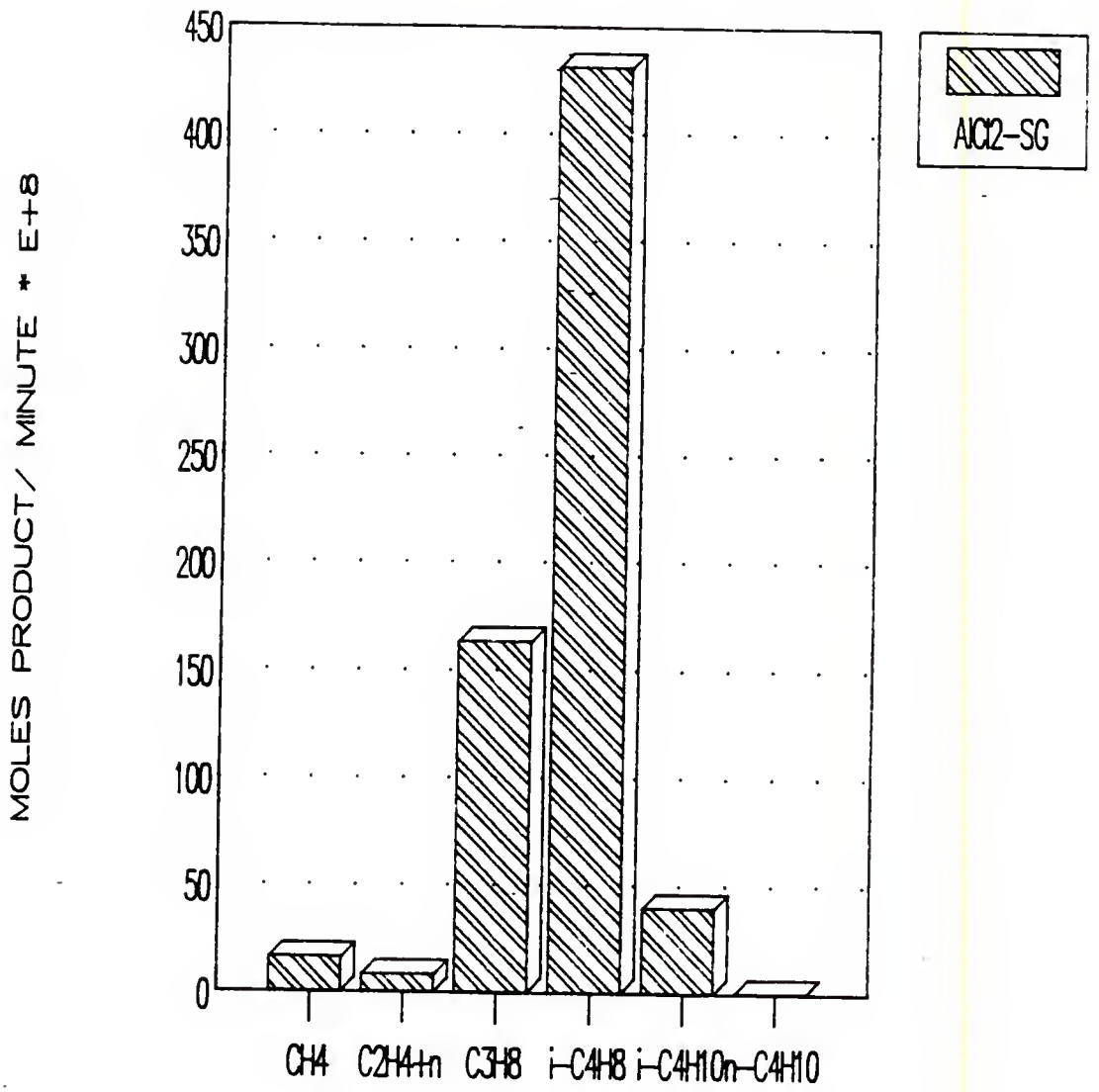


Figure 2-35. Major Products from the Reaction of n-Hexadecane with a Solid Acid Catalyst at 175°C.

quantities of chloroform were detected in the product stream and only trace amounts of carbon tetrachloride were detected. This indicates that the hydrodechlorination of carbon tetrachloride is occurring as well as the cracking of n-hexadecane since the ratio between chloroform and the amount of n-hexadecane converted was much greater than 1:1.

The results of a GC/FTIR experiment run on the product stream of the $Pd(II)Cl_2AlCl_2$-SilicaGel catalyst, n-hexadecane, carbon tetrachloride and hydrogen reaction at 175°C are shown in Figure 2-36. As can be seen in Figure 2-36, C_4-C_9 hydrocarbons are predominate with methylene chloride as well as chloroform being present.

The bar chart in Figure 2-37 represents the product distribution and catalyst activity for the $Pd(II)Cl_2AlCl_2$-SilicaGel catalyst at T= 160 minutes and 175°C. The Pd(II)-doped catalyst shows very high activity for the iso-C_4 alkanes and alkenes as well as a low activity for the undesirable C_1-C_2 products.

A comparison of the catalyst activity and selectivity for the undoped and doped acid catalysts is presented in Figure 3-38. Notice the increase in activity upon switching from an undoped to a metal doped catalyst and the presence of olefins in both product streams. The presence of olefins in the $AlCl_2$-SilicaGel product stream is a strikingly different result than that obtained when a conventional glass flow reactor or a stirred batch reactor is used. When the $AlCl_2$-SilicaGel catalyst is used in a conventional glass flow reactor (vapor phase reactants), or a stirred batch reactor,

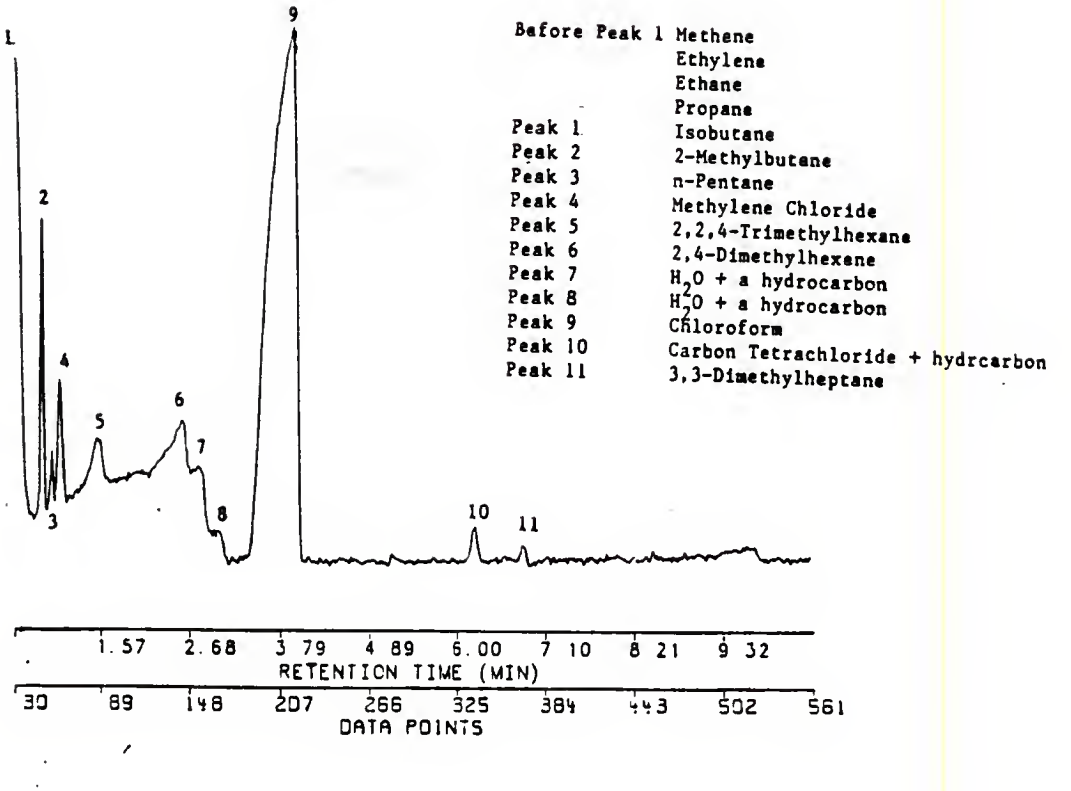

Before Peak 1 Methene
Ethylene
Ethane
Propane
Peak 1 Isobutane
Peak 2 2-Methylbutane
Peak 3 n-Pentane
Peak 4 Methylene Chloride
Peak 5 2,2,4-Trimethylhexane
Peak 6 2,4-Dimethylhexene
Peak 7 H2O + a hydrocarbon
Peak 8 H2O + a hydrocarbon
Peak 9 Chloroform
Peak 10 Carbon Tetrachloride + hydrcarbon
Peak 11 3,3-Dimethylheptane
1.57 2.68 3 79 4 89 6.00 7 10 8 21 9 32
RETENTION TIME (MIN)
30 89 148 207 266 325 384 443 502 561
DATA POINTS

Figure 2-36. GC-FTIR Chromatogram of the Product Stream from the Reaction of a $Pd(II)Cl_2AlCl_2$-SiO_2 Catalyst with n-Hexadecane at 175°C.

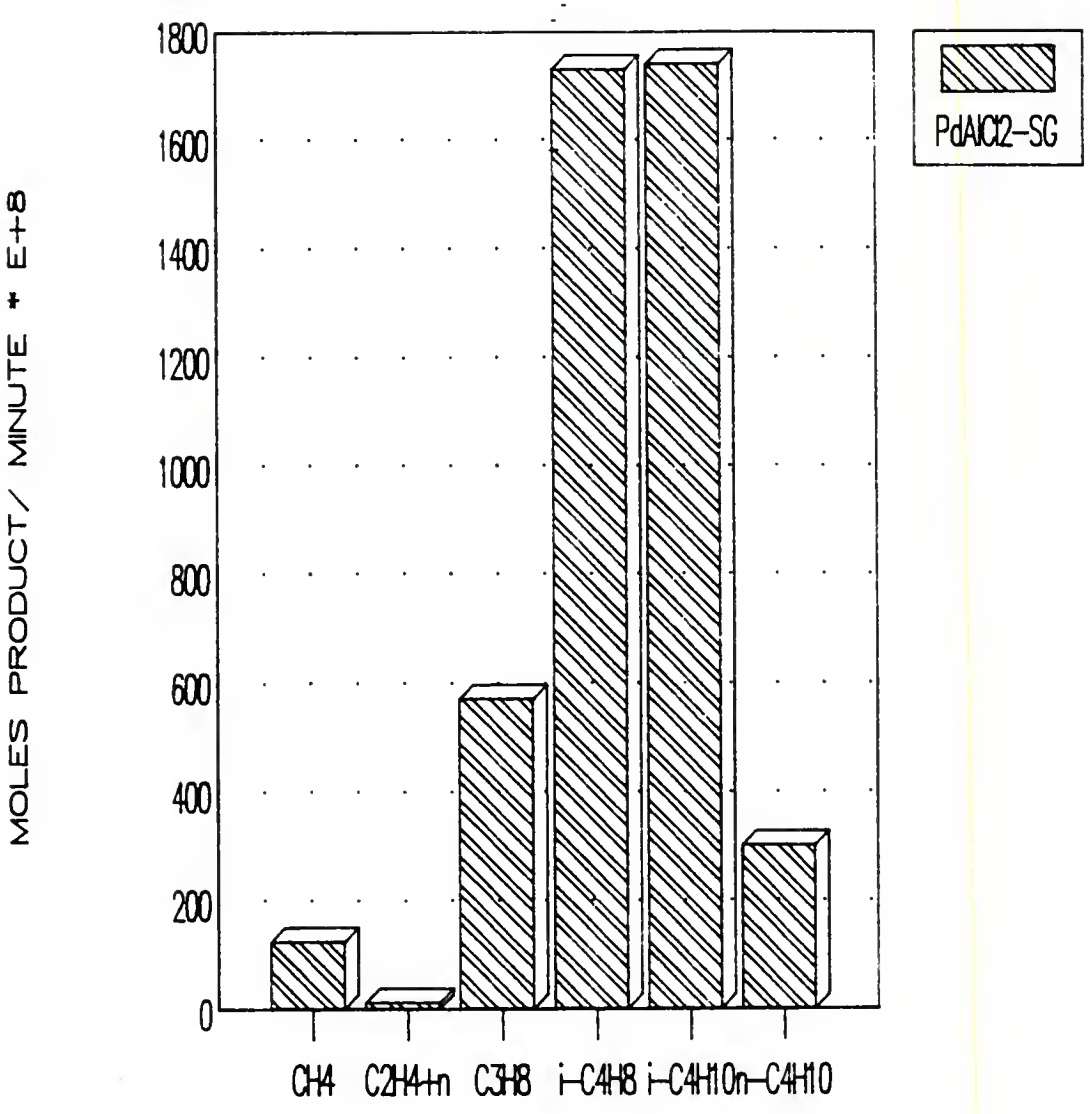


Figure 2-37. Major Products from the Reaction of n-Hexadecane with a $Pd(II)Cl_2AlCl_2$-SiO_2 Catalyst at 175°C.

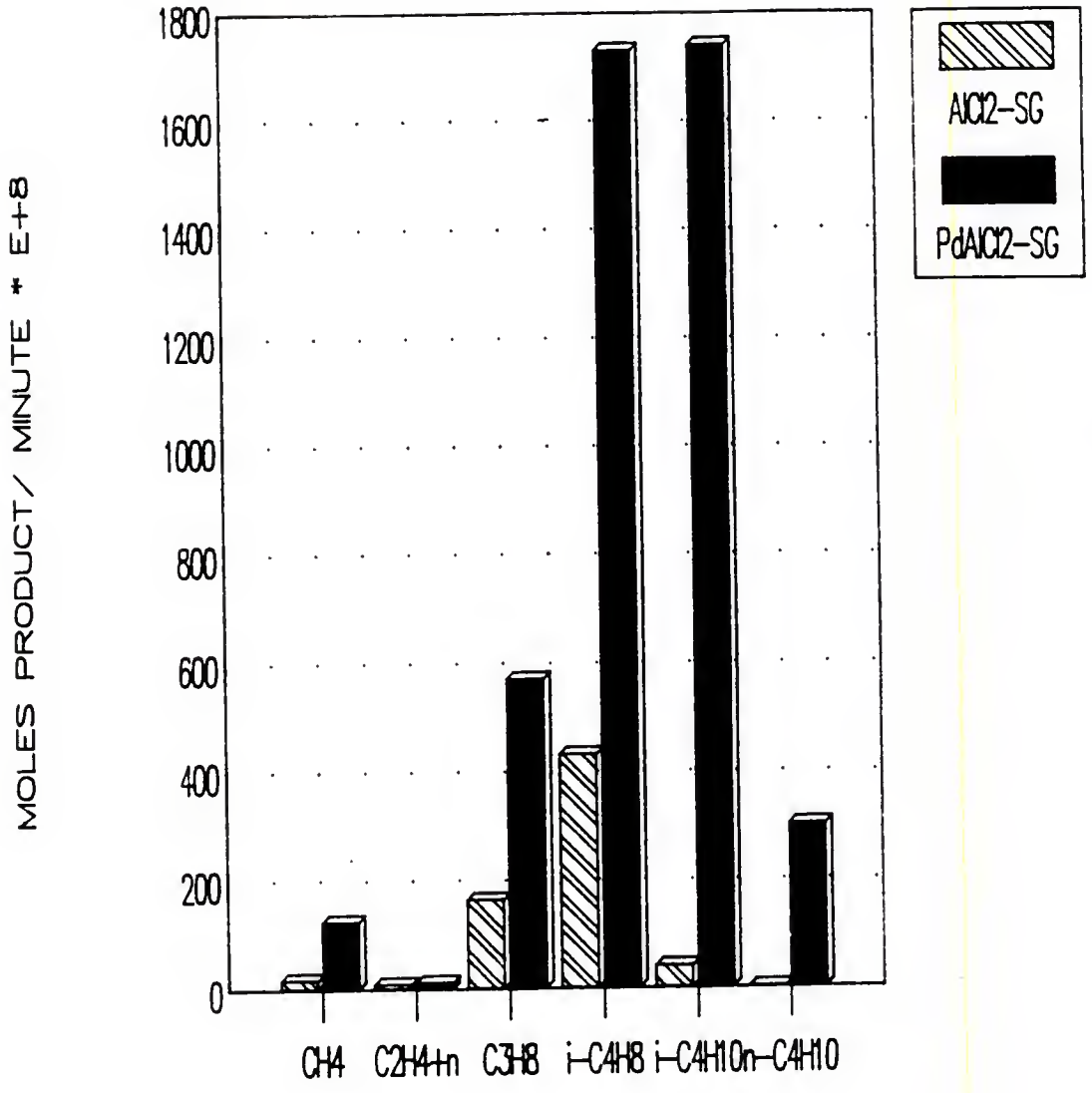


Figure 2-38. Comparison of the $AlCl_2$- and $Pd(II)Cl_2AlCl_2$-SiO_2 Catalysts.

only saturated hydrocarbons are formed. Another striking difference is that when the Pd(II)-doped catalyst is used in a syringe pumped flow reactor almost all of the carbon tetrachloride is converted to $CHCl_3$ or $CHCl_2$.

This increase in cracking activity suggests that the noble metal present in the catalyst is activating molecular hydrogen and producing hydride ion which is then (by spillover) available for the carbonium ion species in the system.[66,67] The increase in the amount of available hydride ion increases the reaction rate and decreases the amount of hydride abstraction from the hydrocarbon substrate. This causes a decrease in the rate of coke formation and subsequently increases the activity as well as the lifetime of the catalyst. The observed results agree with the proposed mechanism and are consistent with the fact that an increase in the concentration of the hydride ion on the catalyst surface would inhibit the adsorption of carbonium ions onto the catalyst surface. The decrease in adsorption of carbonium ions on the surface limits unwanted side reactions such as coke formation. The formation of alkenes in the $AlCl_2$-SiO_2 system arises from the short contact times (fast flow rates) and the larger formation of alkenes in the $Pd(II)Cl_2AlCl_2$-SiO_2 system arises from the dehydrogenation ability of the noble metal on the catalyst.

Since the reactions involving n-hexadecane worked so well and the fact that almost all of the carbon tetrachloride added to the Pd(II)-doped acid catalyst system was converted to $CHCl_3$ or $CHCl_2$, several dehydrochlorination and hydrodechlorination reactions of

various polychlorinated methanes and ethanes were conducted. These reactions will be discussed in the next chapter which is on the dehydrochlorination of various polychlorinated molecules.

Other Acid Catalyzed Reactions Involving Hydrocarbons and Solid Acid Catalysts

Reactions such as polymerizations, alkylations and methane activation are catalyzed by strong acids. These reactions were conducted using the aluminum chloride treated inorganic oxides to determine the scope of reactions that can be catalyzed by the new solid acids.

The polymerization reactions were conducted in a 250 mL Parr pressure apparatus as described in the experimental section. The polymerizations were carried out using carbon tetrachloride and toluene as solvents with the addition of 5 to 15 mL aliquots of monomers. Small aliquots of monomer were used since all the polymerization reactions conducted were very exothermic. The reactions were conducted at room temperature and the monomer used consisted of both radical-only and cationic initiated monomers. Cationic initiated monomers were used to test the acid catalyzed polymerization ability and the radical-only initiated monomers were used to determine if the radical species present on the catalyst surface after preparation were reactive.

The cationic monomers used were styrene, isobutylene, ethyl vinyl ether and 1-hexene. Polymerizations involving styrene monomer resulted in a polymer with an average molecular weight distribution of ~15,000 as determined by Gel-Permeation chromatography which was

conducted with the help of Bill Toreki. Styrene is very easily polymerized and the polymerization of styrene monomer may be initiated by radical, anionic, cationic or metal-complex initiators.[68-70] Since styrene may be polymerized by radical initiators several monomers were used which cannot be polymerized by radical initiators. Isobutylene, 1-hexene and ethyl vinyl ether are monomers which will not polymerize in the presence of radical initiators. These monomers will polymerize in the presence of cationic initiators.

When ethyl vinyl ether, isobutylene or 1-hexene are placed in contact with a solution of carbon tetrachloride or toluene containing 1 gram of the $AlCl_2$-SiO_2 solid acid catalyst, an exothermic reaction takes place and results in the formation of a polymeric material. The results from the polymerization of 1-hexene are shown in Figures 2-39 to 2-40. Shown in Figure 2-39 is the IR spectrum of neat (purified) 1-hexene before polymerization. The carbon-carbon double bond stretching frequency is located at ~1640 cm^{-1} and the carbon-carbon double bond bending frequencies are located at ~990 cm^{-1} and 900 cm^{-1}, respectively. Upon polymerization these bands disappear (Figure 2-40) indicating the reaction of the carbon-carbon double bonds to produce carbon-carbon single bonds. The successful polymerization of 1-hexene, ethyl vinyl ether and isobutylene provides further support for the presence of Bronsted and Lewis acid sites on the solid acid catalysts.

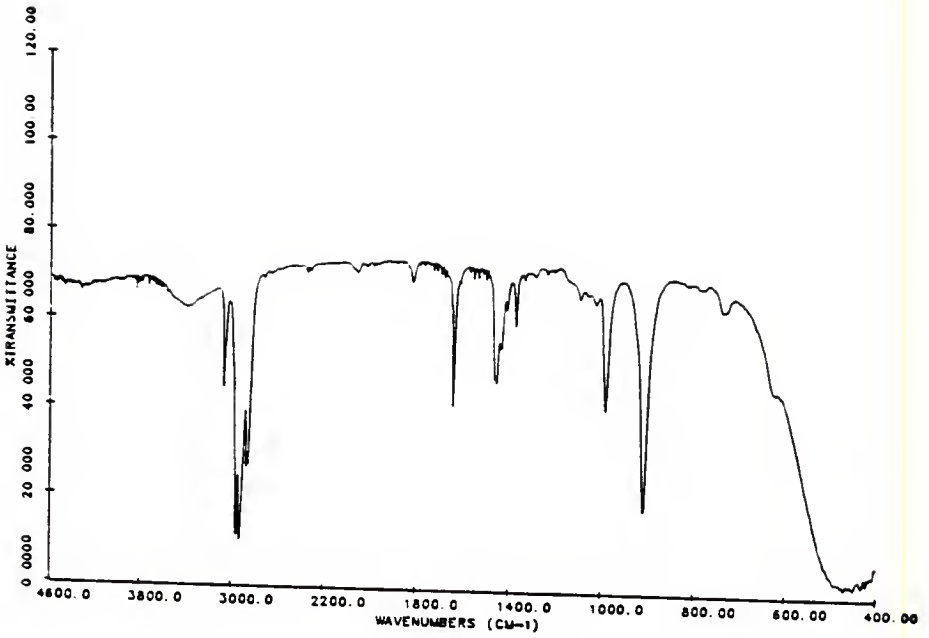


Figure 2-39. Infrared Spectrum of Purified Neat 1-Hexene.

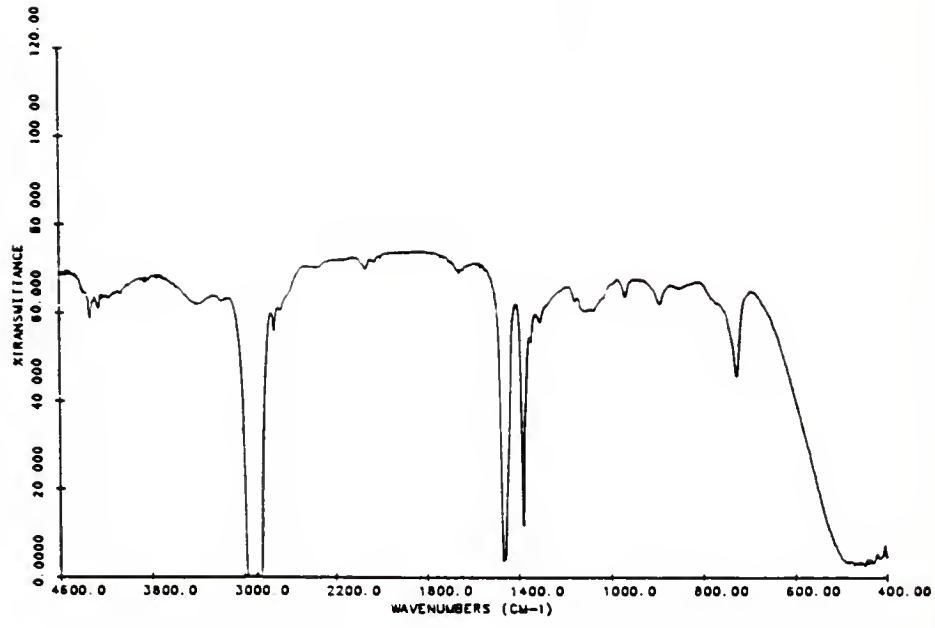


Figure 2-40. Infrared Spectrum of Polymerized 1-Hexene.

Next several monomers that can only be polymerized by radical initiators were used in the polymerization reactions to demonstrate that the radical on the catalyst surface does not contribute to the activity of the catalyst. The monomers used in the polymerization reactions were methyl methacrylate, methacrylate and vinyl acetate. In all cases these monomers did not give rise to any polymer formation indicating that the radical present on the catalyst surface is not a reactive species and does not contribute to the catalyst activity.

In addition to the polymerization of pure monomers an experiment was conducted to produce a co-polymer that contained styrene and methyl methacrylate units. In this experiment a 1:1 molar ratio of styrene and methyl methacrylate was added to a solution of toluene containing 1 gram of an aluminum chloride treated silica gel catalyst prepared in carbon tetrachloride. A polymeric material was isolated from this reaction mixture by filtration to remove the solid acid followed by evaporation of the solvent. When a proton NMR was taken of this material the integrated methyl to aromatic proton resonances were in a ratio of 3:5 which would indicate a 1:1 co-polymer of methyl methacrylate and styrene.

One additional polymerization reaction was conducted using epichlorohydrin as the monomer. Epichlorohydrin is initiated only by strong cationic initiators and there is much interest in the polymerization of epichlorohydrin because the polymer product is used extensively in the aerospace industry as an adhesive. When

epichlorohydrin is added to a solution of toluene containing an aluminum chloride treated silicon dioxide prepared in carbon tetrachloride a polymeric material is formed. The product was identified by IR spectroscopy as poly-epichlorohydrin which was obtained in a 50% yield.

The conclusions from the polymerizations are that the solid acid catalysts prepared by reacting aluminum chloride with inorganic oxides behave similar to other known solid acid catalysts in their polymerization abilities and that the radical present on the catalyst surface does not contribute to the catalyst activity. Since only cationic polymerization activity was observed for the solid acids further investigations involving polymerizations would not be conducted because the chemistry is well known and would not lead to any greater understanding of this solid acid catalyst system.

A new area of research in which strong solid acids and superacids are being used is the activation of methane. It has been demonstrated that when a mixture of C_2-C_4 olefins and methane are passed through a superacid catalyst an exothermic alkylative condensation reaction occurs, (Equation 2-11).[71]

$$CH_4 + RCH{=}CH_2 \longrightarrow CH_3CHRCH_3 \qquad (2\text{-}11)$$

This reaction was confirmed by reacting ^{13}C-labels methane and ethane over a superacid catalyst. The products of this reaction was

the mono-^{13}C-labeled propane and some oligomerization products of the ethylene.

The use of superacid catalysts for the alkylative condensation of methane results in higher selectivity and can be conducted at milder conditions than pyrolytic and free-radical reactions such as combustion, hydrogenation, nitration and sulfochlorination.[71]

Work in the area of alkylative condensation of methane has focused on the use of olefin-methane feeds that do not contain alkanes.[71] The mechanism of the reaction involves protonation of the olefin by the superacid and reaction of the alkyl carbonium ions with methane to form an alkane of one higher carbon number and a proton. Since in the catalytic cracking reactions of alkanes which were discussed earlier in this chapter have been proposed to proceed by hydride abstraction from an alkane to form an alkyl carbonium ion the alkylative condensation of methane was attempted using an alkane substrate.

The catalyst used for the alkylation condensation of methane was the $Pd(II)Cl_2AlCl_2$-SiO2 catalyst used for the catalytic cracking of n-hexadecane earlier in this chapter. The reaction was conducted in a syringe pump flow reactor with a methane flow rate of 51 cc/minute, n-pentane flow rate of 0.005 cc/minute, a carbon tetrachloride flow rate of 0.005 cc/minute and a reaction temperature of 175°C. After the reaction was allowed to proceed for several hours pregas and post gas samples were collected from the reactor. The GC traces for pregas and post gas samples are shown in Figures 2-41 and 2-42. Methane is the only product in the pregas

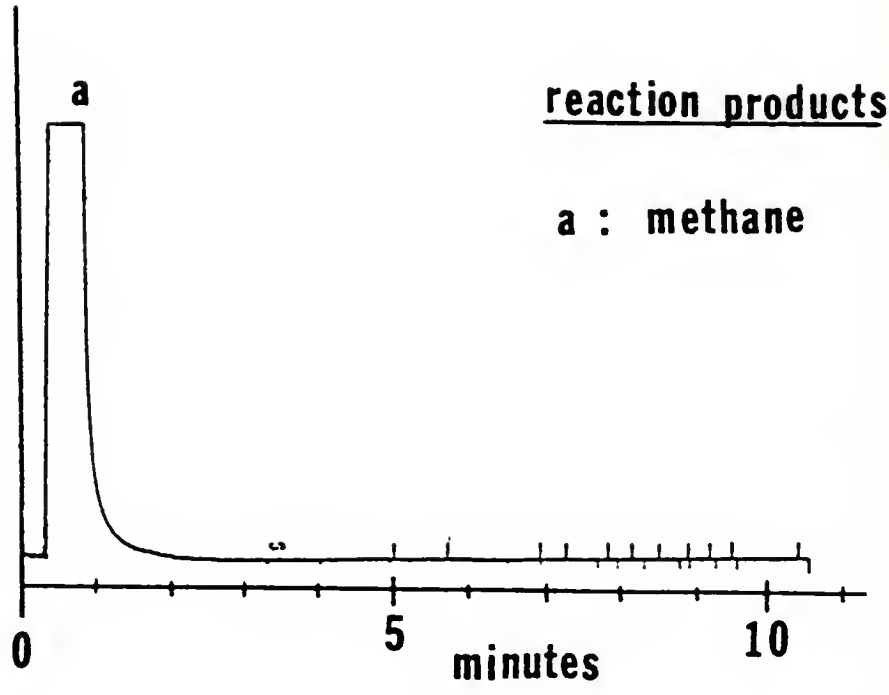


Figure 2-41. Pregas Sample for the Alkylative Condensation of Methane by a Solid Acid Catalyst.

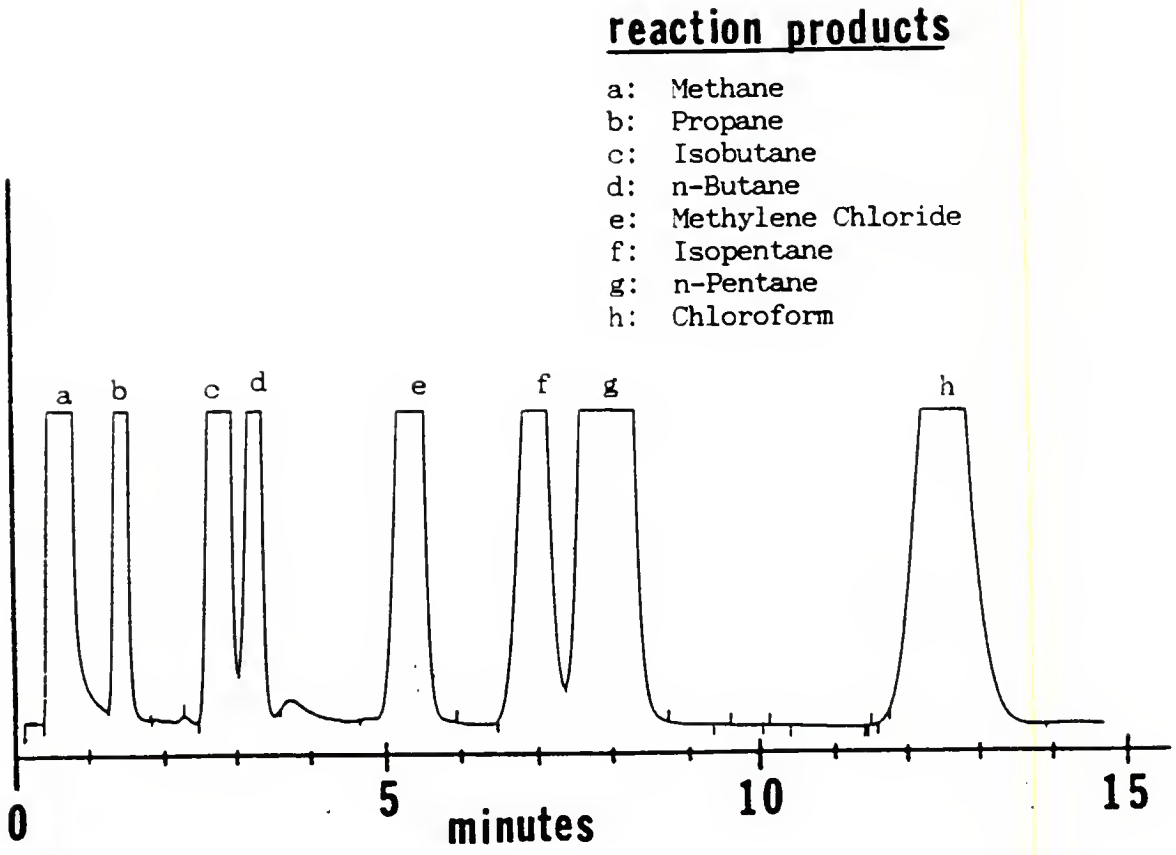


Figure 2-42. Post Gas Sample for the Alkylative Condensation of Methane by a Solid Acid Catalyst at 175°C.

sample while a large quantity of C_3-C_5 hydrocarbons, methylene chloride and chloroform are present in the product stream. In observing the product distribution it is apparent that a peak due to C_2 products which would occur at 1 minute is missing. The absence of the peak due to ethylene is an indication that the ethyl carbonium ions produced in the reaction have reacted with the methane to produce propane. Also when the number of moles of methane in the pregas and post gas are compared a decrease in the number of moles of methane is observed indicating that an alkylative condensation of methane has occurred. When a blank reaction is conducted with only methane and carbon tetrachloride as the reactants no products are observed.

To demonstrate that ethylene is produced during the cracking of n-pentane the methane feed was stopped and a hydrogen feed was started. After several hours of reaction pregas and post gas samples were collected. The GC traces for the post gas sample is shown in Figure 2-43. Only trace quantities of methane were observed in the pregas and as expected ethylene was present in the product stream indicating that in the presence of excess hydrogen the alkyl carbonium ions are easily quenched to form the corresponding alkanes. However, when the cracking reaction is conducted in the presence of excess methane and no hydrogen is present the alkyl carbonium ions undergo an alkylative condensation reaction with methane to produce alkanes with an increased chain length.

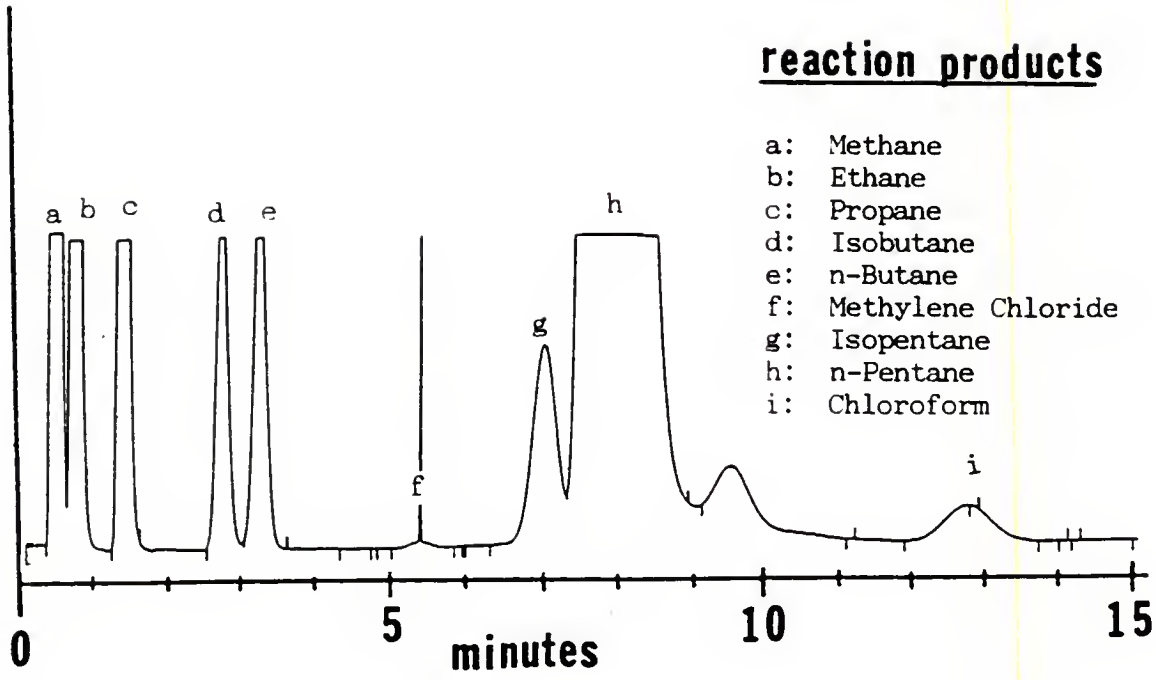


Figure 2-43. Post Gas Sample for the Cracking of n-Pentane at 175°C.

To further investigate the alkylative condensation of methane using alkanes as the substrate a reaction involving ethane was conducted. A $Pd(II)Cl_2AlCl_2$-SiO_2 catalyst was reacted with ethane in excess methane at 175°C. Only a trace amount of propane was observed in the product stream and in the same amount as that in the pregas. This result suggests that the Lewis acid sites present on the catalyst are not strong enough to abstract a hydride ion from ethane or methane. The propane produced in the earlier experiments was a result of the ethyl carbonium ions produced during the cracking of n-pentane. Since there are Bronsted acid sites present that are capable of protonating olefins (as described in the polymerization section) the solid acid catalyst could be used in the same manner as the superacid catalysts by reacting C_2-C_4 olefins in excess methane.

What has been learned from the alkylative condensation reactions is that the solid acid catalyst exhibits catalytic activity similar to conventional superacids for the reaction of olefins. The area that the solid acid differs from the superacids is in the activation of alkanes for the catalytic cracking of hydrocarbons. The catalytic cracking reaction requires hydrogen and it was the object of the methane activation work to use methane as the hydrogen source in the presence of a solid acid catalyst.

During the catalytic cracking process any primary alkyl carbonium ions formed can react with methane via alkylative condensation to form hydrocarbons with longer chain lengths. Since the evolution of primary carbonium ions during a catalytic cracking

reaction is unfavorable, due to the high energy of these species, the conversion of methane to higher hydrocarbons is only a minor reaction. As a result, the use of methane as a hydrogen source during a catalytic reaction would cause a hydrogen deficient reaction system that would promote coke formation and decrease catalyst activity and stability.

When the alkylative condensation of methane was conducted with trace amounts of ethylene no products were observed. As the concentration of ethylene was increased products were detected in the product stream, The major products of the reaction were isobutane, n-butane, isopentane, n-pentane and isomers of hexane. A small amount of propane was detected and the formation of coke was evident.

Next the methane feed was stopped and hydrogen was added to the reaction system. GC analysis of the product stream revealed no change in the selectivity of the reaction systems. The catalyst activity did increase upon addition of hydrogen indicating that under a methane atmosphere the reaction system was hydrogen deficient.

2.4 SUMMARY

The main goal of this investigation was to prepare a solid acid with stable tetrahedral sites. Using aluminum chloride as a precursor, solid acid catalysts were prepared by the reaction of inorganic oxides with aluminum chloride in refluxing carbon

tetrachloride. The catalysts were characterized by IR and NMR spectroscopy. The infrared spectrum of adsorbed pyridine was used to probe the nature and strength of the acid sites present on the catalysts. The infrared spectrum of adsorbed pyridine on the various aluminum chloride treated inorganic oxides ($AlCl_2$-X; where X= inorganic support) indicated the presence of both Lewis and Bronsted acid sites. Large shifts (18 cm^{-1}) were observed for coordinated pyridine when X= SiO_2 or a high silica zeolite. When the aluminum chloride treated inorganic oxides are prepared in solvents other than carbon tetrachloride the resulting solid materials exhibit lower acidity which is reflected in the lower frequency shifts for adsorbed pyridine.

Through the use of ^{27}Al and ^{29}Si solid-state MAS NMR spectroscopy it has been shown that the aluminum chloride retains its tetrahedral conformation upon reaction with the inorganic oxide support.

The new strong solid acid catalyst system exhibits high catalytic activity and selectivity for cracking reactions under relatively mild conditions. The trend in the catalytic activity of the solid acid catalysts parallel the trend in the frequency shifts in the infrared spectrum of absorbed pyridine.

Reactions such as polymerization and methane activation are catalyzed by strong acids. These reactions were conducted using the aluminum chloride treated inorganic oxides to determine the scope of reactions that can be catalyzed by the new solid acids. Results of the polymerization data suggest that the solid acid catalysts behave

similarly to other known solid acid catalysts in their polymerization abilities and that the radical present on the catalyst surface does not contribute to the catalyst activity. Results obtained from the alkylative condensation of methane suggest that direct activation of methane or ethane by the aluminum chloride treated inorganic oxides does not occur. The activation of methane by the solid acid catalysts may only occur by reaction of methane with ethyl carbonium ions generated through the cracking of higher chain hydrocarbons. The activation of methane by this method occurs only in small quantities (<1%).

CHAPTER III
REACTIONS OF CHLORINATED HYDROCARBONS

3.1 BACKGROUND

Organochlorine compounds are extremely important in today's society. These compuonds are widley used in many areas of technology due to their various physical and chemical properties.[72] Industries that use organochlorine compounds are the plastic and synthetic fibers industry, resin industry, mechanical engineering, electronics, metal-processing, pharmaceutical chemical industry, and domestic chemistry. Organochlorine monomers such as vinyl chloride are polymerized into polymers and used in the production of rubbers, foamed materials, phonograph records, and paint and varnish materials.[72,73]

Chloromethanes have also come into wide use.[72] Methyl chloride is used as a reactant in the organosilicon industry and methylene chloride is used in the production of cellulose triacetate. Chloroform is the starting material for a whole class of freons and is also used extensively as a solvent. Carbon tetrachloride, which is produced in the largest quantity, is used extensively in the chlorofluorocarbon industry for the production of freons.[73] Carbon tetrachloride also finds use as a solvent,

an extractant, a defatting agent, a fumigant, a fire-extinguishing agent, and a rubber vulcanization accelerator. Polychloroethanes and polychloroalkenes have found extensive use in industry as solvents, cold cleaners, vapor degreasers, and dry cleaners.[74,75] Extensive work has been performed on the chemical transformation of organochlorine compounds because of the large quantities of organochlorine compounds that are used. Currently, research has focussed on the areas of dehydrochlorination and hydrodechlorination.[76-81]

The investigation of the dehydrochlorination and hydrodechlorination processes is important because many organochlorine compounds are produced by these reactions.[76-78] The dehydrochlorination process is the selective removal of HCl from a molecule. The reaction of 1,2-dichloroethane to form vinyl chloride and HCl would be an example of this reaction. At present, vinyl chloride is commercially produced by the thermal dehydrochlorination of 1,2-dichloroethane and no catalytic process is employed.[73]

The hydrodechlorination process is the selective replacement of a chlorine atom with a hydrogen atom. An example of this reaction is the conversion of carbon tetrachloride to chloroform. The hydrodechlorination process is not used extensively in industry for the production of organochlorine compounds. The main interests in hydrodechlorination are in kinetic and mechanistic studies and the decomposition of hazardous or unwanted organochlorine compounds to more useful products.[77,78,80-82]

Many catalysts have been investigated for the dehydrochlorination and hydrodechlorination of organochlorine compounds.[75-83] The catalysts range from Group VIII metals on solid supports to homogeneous organometallic complexes. Disadvantages of the catalysts are that they proceed via a radical type mechanism, are not selective to the desired products, form high molecular weight polychlorinated hydrocarbons, and catalyst activities last for only a very short time.[77-81] The disadvantages of the dehydrochlorination and hydrodechlorination catalysts are similar to those found for the hydrocarbon cracking catalysts. As a result the new metal-doped solid acid catalysts developed in the last chapter for the cracking of hydrocarbons were used for the dehydrochlorination and hydrodechlorination of various polychlorinated molecules.

When carbon tetrachloride or tetrachloroethylene were used as chlorine sources for the catalytic cracking runs, products were observed which correspond to the replacement of a carbon-chlorine bond by a carbon-hydrogen bond. The objective of this research was to explore the chemistry of the Group VIII metal-doped solid acid catalysts organochlorine compounds and to determine if metal doped solid acids can be used as effective dehydrochlorination and hydrodechlorination catalysts.

For the hydrodechlorination reactions, carbon tetrachloride was chosen as one of the model compounds because much work has already been performed on this reactant and due to the fact that carbon tetrachloride is produced in large volumes.[77,79-81]

A major use of carbon tetrachloride is in the production of chloroflourocarbons that have been linked to the depletion of the Earth's ozone layer.[73] The conversion of carbon tetrachloride to chloroform is of interest due to the fact that a decrease in carbon tetrachloride comsuption is expected arising from the ban placed on certain chlorofluorocarbons. The feed stock for the new generation of chlorofluorocarbons (that are not hazardous to the Earth's ozone layer) will be based on chloroform rather than carbon tetrachloride.

For the dehydrochlorination reactions 1,2-dichloroethane was chosen as the model compound because one of the largest industrial dehydrochlorination reactions is the dehydrochlorination of 1,2-dichloroethane to produce vinyl chloride. No commercial process currently used to make vinyl chloride employs catalysis.

The following chapter is concerned with the preparation of various Group VIII metal-doped solid acid catalysts and their use as dehydrochlorination and hydrodechlorination catalysts for the chemical transformation of low-value or waste organochlorine compounds to more useful organochlorine or hydrocarbon products.

3.2 EXPERIMENTAL

Reagents

All metal halides were used as purchased unless otherwise stated. The palladium (II) chloride ($PdCl_2$), dipotassium tetrachloro pallidate (K_2PdCl_4), ruthenium (III) chloride ($RuCl_3$),

copper (II) chloride ($CuCl_2$), cobalt (II) chloride ($CoCl_2*6H_2O$) and rhodium (III) chloride ($RhCl_3$) were purchased from Aldrich Chemical Company. Aluminum chloride (Al_2Cl_6) was purchased from Alfa Products with a purity of 99.997%. All metal carbonyls were used as purchased unless otherwise stated. The dicobalt octacarbonyl, tetracobalt dodecacarbonyl, hexarhodium hexadecacarbonyl and triruthenium dodecacarbonyl were purchased from Strem. All solvents were purchased from Fisher Scientific except tetrachloroethylene which was purchased from Kodak. Carbon tetrachloride, chloroform and methylene chloride were dried over phosphorous (V) oxide (Fisher). Chloroform (containing ethanol as a stabilizer) was purified by passage through an activated alumina column. Tetrachloroethane, 1,2-dichloroethane, n-pentane, 2,6-dichloroanisole and diphenyl ether were used as purchased. Gold label (99+%) pyridine was purchased from Aldrich and was used without further purification. All solvents were stored over 4 A molecular sieves (Davison). The gaseous reactants methane, ethane, propane, methyl chloride and technical grade hydrogen chloride (99.0%) were purchased from Matheson. Hydrogen, Helium, argon and nitrogen were supplied by Airco and Liquid Air. The Semiconductor Grade hydrogen chloride (99.995%) was purchased from Air Products. The support used for the preparation of the catalysts was silicon dioxide (SiO_2). The support material was used as purchased unless otherwise stated. The primary material was Davison Grade #62 silicon dioxide (donated by W.R. Grace Co.) with a surface area of 340 m^2/gram, pore volume of 1.1 cm^2/gram

and a mess size of 60-200.[35] The sodium cyanide was obtained from Fisher Scientific and used as purchased. The benzyl dimethylstearly ammonium chloride monohydrate, Aliquot 336 and tetraheptyl ammonium bromide were purchased from Aldrich Chemical Company.

Preparation of a Palladium (II) Chloride-Aluminum Chloride Doped Catalyst Using Carbon Tetrachloride as a Solvent

In a 200 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 5.0 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs), 0.06 grams palladium (II) chloride ($PdCl_2$) and 100 mL of carbon tetrachloride (dried over 4 A sieves). The reaction mixture was stirred and heated at reflux under a nitrogen (N_2) atmosphere for 6 hours. Next 2.61 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 2 days.

After 2 days the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was orange in color.

The catalyst was water-sensitive and turned light peach on exposure to moisture.

Preparation of a Rhodium (III) Chloride-Aluminum Chloride Doped Silica Gel Catalyst Using Carbon Tetrachloride as a Solvent

In a 200 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 9.0 grams of a 2% rhodium (III) chloride ($RhCl_3$) on silica gel (prepared as above for palladium), 5.0 grams aluminum chloride, and 150 mL of carbon tetrachloride (dried over 4 A sieves).The reaction mixture was allowed to stir at reflux under a N_2 atmosphere for 24 hours.

After 24 hours the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was orange in color.

The catalyst was water-sensitive and turned light orange on exposure to moisture.

Preparation of a Dipotassium Palladium (II) Chloride-Aluminum Chloride Doped Catalyst Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 15.2 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs), 0.347 grams dipotassium palladium (II) chloride (K_2PdCl_4) and 150 mL of carbon tetrachloride (dried over 4 A sieves). The reaction mixture was stirred and heated at reflux under a nitrogen (N_2) atmosphere for 6 hours. Next 7.8 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 24 hours.

After 24 hours the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was peach in color.

The catalyst was water-sensitive and turned white on exposure to moisture.

Preparation of a Ruthenium (III) Chloride-Aluminum Chloride Doped Catalyst Using Carbon Tetrachloride as a Solvent

In a 300 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 10.02 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs), 0.164 grams ruthenium (III) chloride ($RuCl_3$) and 150 mL of carbon tetrachloride (dried over 4 A sieves). The reaction mixture was stirred and heated at reflux under a nitrogen (N_2) atmosphere for 5 hours. Next 5.0 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 24 hours.

After 24 hours the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was orange in color.

The catalyst was water-sensitive and turned white on exposure to moisture.

Preparation of a Copper (II) Chloride-Aluminum Chloride Doped Catalyst Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 15.1

grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs), 0.235 grams copper (II) chloride ($CuCl_2$) and 150 mL of carbon tetrachloride (dried over 4 A sieves). The reaction mixture was stirred and heated at reflux under a nitrogen (N_2) atmosphere for 6 hours.

Next 8.2 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 24 hours.

After 24 hours the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was yellow in color.

The catalyst was water-sensitive and turned white on exposure to moisture.

Preparation of a Cobalt (II) Chloride-Aluminum Chloride Doped Catalyst Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 15.0 grams of silica gel (washed with 1M HCl and dried under vacuum at 80°C for 72 hrs), 0.278 grams cobalt (II) chloride ($CoCl_2*6H_2O$) and 150 mL of carbon tetrachloride (dried over 4 A sieves). The reaction mixture was stirred and heated at reflux under a nitrogen (N_2) atmosphere for 6 hours.

Next 8.4 grams of anhydrous aluminum chloride (Al_2Cl_6) was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 24 hours.

After 24 hours the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was blue in color.

The catalyst was water-sensitive and turned white on exposure to moisture.

Preparation of a Iron (III) Chloride-Aluminum Chloride Doped Catalyst Using Carbon Tetrachloride as a Solvent

In a 250 mL 3-neck round bottom flask equipped with a reflux condenser and a teflon coated magnetic stir bar was placed 15.8 grams of a $FeCl_2$-SiO_2 catalyst (prepared the same as the $AlCl_2$-SiO_2 catalyst reported in chapter II), 7.6 grams aluminum chloride and 100 mL of carbon tetrachloride (dried over 4 A sieves). The reaction mixture was stirred and heated at reflux under a nitrogen (N_2) atmosphere for 24 hours.

After 24 hours the reaction mixture was filtered under an N_2 atmosphere. The filtrate was colorless and the resulting solid product obtained was brown in color.

The catalyst was water-sensitive and turned light brown on exposure to moisture.

3.3 RESULTS AND DISCUSSION

Heterogeneous Hydrogenation of C-Cl Bonds

When carbon tetrachloride or tetrachloroethylene were used as chlorine sources for the catalytic cracking runs products were observed which correspond to the replacement of a carbon-chlorine

bond with a carbon-hydrogen bond. In order to more fully explore this chemistry a palladium(II)-doped acid catalyst was prepared with the aim of catalytically and selectively converting CCl_4 to $CHCl_3$. Palladium was chosen because it is known that palladium will activate dihydrogen and form hydrogen atoms on the catalyst surface which can then be used to replace a chlorine on carbon tetrachloride.[83]

The experiments to determine catalytic activity for the palladium-doped catalyst were conducted in a heterogeneous glass flow reactor as described in the previous chapter. A hydrogen gas feed saturated with carbon tetrachloride vapors was passed over the catalyst at 90°C and atmospheric pressure. Table 3-1 gives a summary of the product distribution for the reaction of $Pd(II)AlCl_2SG$ with H_2 and CCl_4 at 90°C. At 90°C the catalyst produces chloroform with high selectivity. To determine whether the Pd doped catalyst was performing the actual catalysis two blank reactions were carried out. The first experiment involved the use of the undoped catalyst with an H_2 and CCl_4 feed at 90°C. Only two trace products were detected which might have been phosgene and HCl. No chloroform was detected even at 140°C and any other products formed were in trace amounts. The second blank reaction involved the use of 3% palladium-on-charcoal. This was to determine if only palladium was required to carry out the reaction. Table 3-2 gives a summary of the product distribution for the reaction of 3% palladium-on-charcoal with H_2 and CCl_4 at 90°C. A wide variety of products are formed in this reaction.

Table 3-1. Product Distribution for Pd(II)$AlCl_2$-SiO_2 Catalyst at 90°C with H_2 and CCl_4.

PRODUCT	AREA	% PRODUCT
Unknown	5871	0.019
Methane	78492	0.252
Phosgene	60493	0.194
HCl	56467	0.181
Methyl Chloride	21831	0.070
Chloroform	3.0932 E+7	99.285

Table 3-2. Product Distribution for a 3% Palladium-on-Charcoal Catalyst at 90°C with H_2 and CCl_4.

PRODUCT	AREA	% PRODUCT
Methane	1109700	12.218
Ethane	1210900	13.333
Propane	340890	3.753
Butane	100530	1.107
Pentane	100780	1.110
Chloroform	6219500	68.479

The C_1 to C_5 hydrocarbons arise from the hydrogenation of the charcoal support and the presence of $CHCl_3$ as a product indicates that only palladium is needed for the conversion of CCl_4 to $CHCl_3$.

The palladium (II) doped acid catalyst has been produced by two different methods and the types of products observed from each catalyst's reaction with carbon tetrachloride are different. The first method of preparation (method I) involved treating a $Pd(II)Cl_2$ doped silica gel with aluminum chloride in refluxing carbon tetrachloride. This type of catalyst will be refered to as an Al_2Cl_6 treated $Pd(II)Cl_2$-SiO_2 catalyst.

The second method of preparation (method II) involved taking a premade batch of Al_2Cl_6 treated silica gel ($AlCl_3/SiO_2$) and doping the catalyst with $Pd(II)Cl_2$. This catalyst will be refered to as a $Pd(II)Cl_2$ doped $AlCl_3/SiO_2$ catalyst. Other catalysts prepared by these methods will be refered to in a similar manner.

As stated previously the catalyst prepared by method I showed high catalytic activity and selectivity for the formation of chloroform from carbon tetrachloride. The catalyst prepared by the second method displayed quite different activities and selectivities. Typical reaction conditions involved placing ~1 gram of the Pd(II)-doped catalysts in a glass flow reactor system and passing hydrogen gas saturated with carbon tetrachloride at various temperatures. A plot of activity versus time for the reaction of a $Pd(II)Cl_2$ doped $AlCl_3/SiO_2$ catalyst with carbon tetrachloride and hydrogen at 90°C and 1 atm pressure is show in Figure 3-1.

For the first few hours only methane was produced. After 4.5 hrs ethane and propane appeared as products with isobutane starting to be produced after 5 hrs. Large amounts of C_1-C_4 products were produced during the first 18 hrs of operation however no chloroform was observed in the product stream. After 18 hrs of reaction chloroform was observed in the product stream in small amounts and the catalyst was still very active for the C_1-C_4 hydrocarbons. The catalyst activity remained stable for 43 hrs at which time the temperature of the reactor was raised to 100°C. No significant increase in chloroform production was seen and the temperature was raised to 110°C. At 110°C hydrocarbon production decreased and the amount of chloroform produced was decreased.

Next the experiment was repeated at 50°C using ~1 gram of the $Pd(II)Cl_2$ doped $AlCl_3/SiO_2$ catalyst to determine if chloroform could be produced at lower temperatures. Thirty minutes after starting the reaction small amounts of methane and ethane were detected. Trace amounts of propane and isobutane were detected and no chloroform was produced. After 2.25 hrs the activity of the catalyst for C_1-C_4 hydrocarbons was increasing and a trace amount of chloroform was observed. By 3 hrs catalyst activity for the C_1-C_4 hydrocarbons had reached a stable level and the catalyst activity for chloroform was increasing. At 5 hrs the amount of

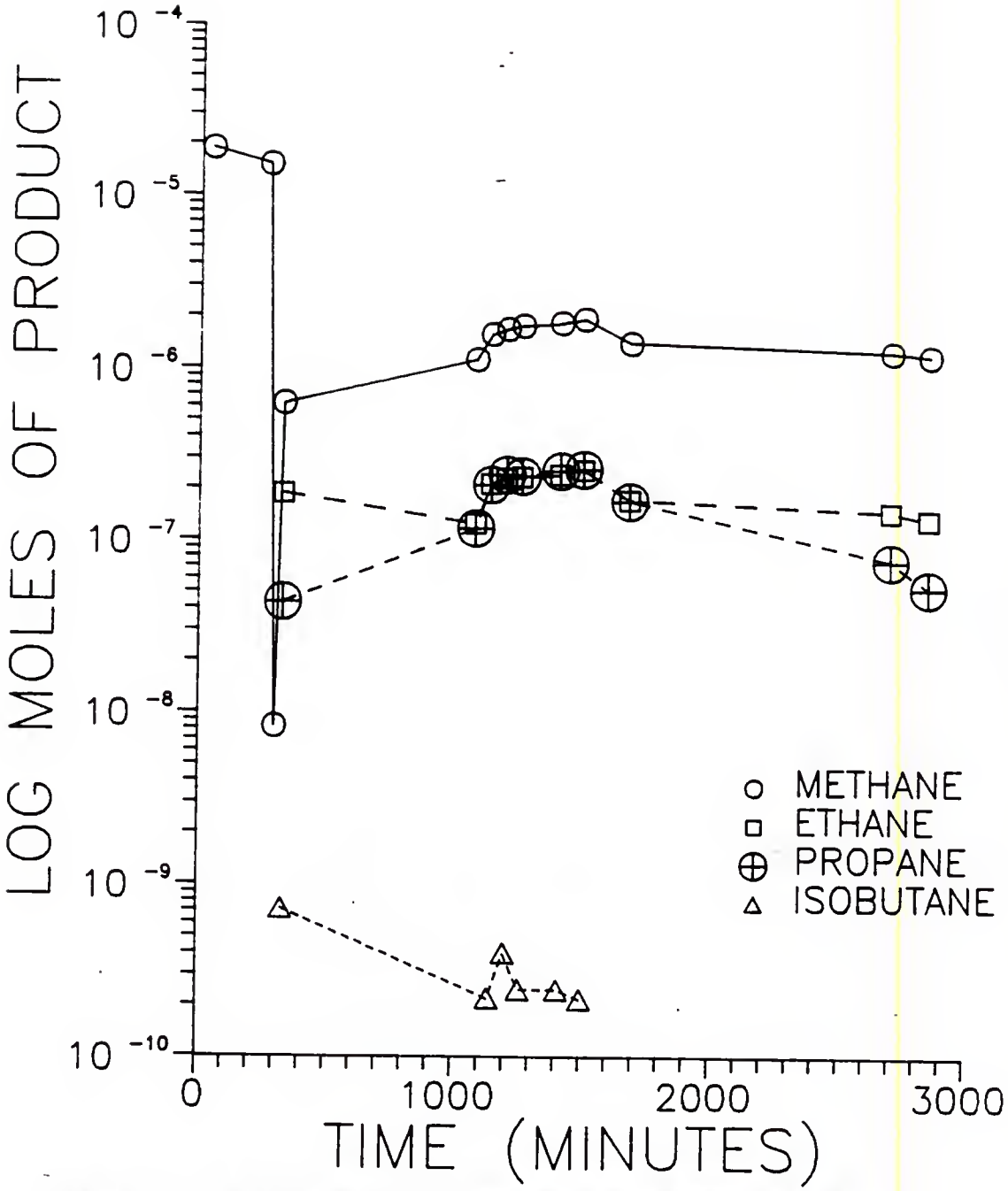


Figure 3-1. Plot of Activity vs Time for the Reaction of $Pd(II)Cl_2AlCl_2$-SiO_2 Catalyst with CCl_4 and H_2 at 90°C.

chloroform in the product stream was 6.4% by area and after 9 hrs chloroform represented 10.1% of the products.

Because of the low percent conversion of carbon tetrachloride to chloroform by the catalyst prepared by method II the catalyst prepared by method I was retried. The catalyst that was prepared by method I appeared as though it had been slightly decomposed by contact with water but a decision was made to try the catalyst to determine if the decomposition product [Pd(II)-on-silica gel] would be an active catalyst. The catalyst was run in the temperature range of 50°C to 150°C and the products monitored by GC. At the lower temperatures (50°C to 90°C) C_1-C_4 hydrocarbons and trace quantities of chloroform were produced. At the higher temperatures (120°C to 150°C) only trace amounts of C_1-C_4 hydrocarbons were produced. This gave some indication that the support was playing a role in the formation of chloroform. When blank reaction was conducted using a Pd(II)-on-silicagel catalyst (prepared without aluminum chloride) no products were observed even at 225°C.

If the undoped acid catalyst is reacted with carbon tetrachloride and hydrogen no activity is observed. When carbon tetrachloride and hydrogen are reacted with a 3% Pd-on-carbon catalyst C_1-C_4 hydrocarbons and chloroform are produced. At this point in time it is known that the Pd(II) doped catalyst is capable of producing chloroform from carbon tetrachloride selectively and work is needed in getting the correct catalyst composition and the best method for preparing the catalyst. The

next step is to look at the role of Pd(II) versus Pd(0) as in our Pd(II)-doped catalyst versus the 3% Pd-on-carbon and look at what effect prereducing our catalyst would have on catalytic activity.

In addition to using the Pd(II)-doped acid catalyst for hydrodechlorination reactions it would be advantageous to use this catalyst in hydrocracking or hydroreforming reactions. Typical reaction conditions include ~1 gram of $Pd(II)Cl_2$ doped $AlCl_3/SiO_2$ catalyst contacted with hydrogen saturated with n-heptane and carbon tetrachloride at 90°C. The catalyst was very active for the cracking of n-heptane but no significant differences in the product distribution was noticed until after 30 hrs into the reaction. After 30 hrs olefins as well as paraffins were produced. High catalytic activity was maintained for 52 hrs before the reactor was shut down. The appearance of the catalyst was only slightly changed after use. The color had turned from light yellow to a darker yellow-brown indicating some build-up of coke. It should be noted that when an undoped catalyst is used in this reaction the catalyst cokes up and turns black in appearance and at no time during the reaction are any olefins produced. The fact that olefins are not produced until after 24 hrs indicates that some transformation is occurring on the catalyst surface to form a palladium species [maybe Pd(0)] which can then dehydrogenate paraffins. This indicates that the role of the Pd(II) or Pd(0) in the reaction of hydrocarbons or chlorinated paraffins needs to be looked at more closely to determine what the best catalyst composition would be for each reaction.

The next set of experiments were conducted to determine the role of the metal in the reaction system and to determine whether the dehydrochlorination or hydrodechlorination reaction was dominant. The chlorinated molecules involved are carbon tetrachloride and 1,2-dichloroethane. All experiments were conducted in the syringe pumped flow reactor system using a pulse technique. This involves pulsing the reactant feed by adding the reactant for a 30 or 60 minute interval and then shutting the feed off and allowing the system to purge at reaction temperature. The purging of the system allows excess solvent which may not have been volatilized during the addition process to be removed. This keeps the catalyst from being soaked in one reactant which many impede the reaction.

A typical experiment may last up to 4000 minutes and consist of 20 to 25 pulses. Reaction temperatures range from 80 to 225°C and flow rates of 1 mL/2 seconds to 1 mL/50 seconds are common. All catalysts used were fine powders except a Pd-on-alumina catalyst obtained from Dr. Ben Huie which was 1/16 inch spheres. One of the first catalysts used was the Pd-on-alumina catalyst obtained from Vulcan and was used in the sphere form. The reaction was conducted by passing hydrogen and carbon tetrachloride over 3.2 grams of a Pd-on-alumina catalyst at 100°C. The Pd-on-Alumina catalyst was very active for producing C_1-C_5 hydrocarbons with methane the predominant product. When the reaction temperature was raised to 150°C catalyst activity dropped slightly but product distribution remained the same. As the

reaction temperature was raised to 175°C and 200°C, catalyst activity increased back to the original level observed at 100°C and chloroform was detected as a reaction product. At all reaction temperatures some methylene chloride was detected in the product stream. The formation of hydrocarbons by the use of a Pd-on-alumina catalyst does not sound unreasonable and confirms palladiums role in the formation of hydrocarbons in the palladium-doped acid catalyst system. Earlier, it was stated that a $Pd(II)Cl_2$-doped acid catalyst prepared by the reaction of $Pd(II)Cl_2$ with silica gel and subsequent reaction with aluminum chloride (method I) resulted in a catalyst which was active for the production of chloroform from carbon tetrachloride . This catalyst did not form much hydrocarbon products from the carbon tetrachloride feed. However, when a $Pd(II)Cl_2$-doped acid catalyst prepared by the reaction of $Pd(II)Cl_2$ with an $AlCl_2$-SilicaGel catalyst (method II) was used for the hydrodechlorination of CCl_4 the major products of the reaction were hydrocarbons with only small amounts of chloroform and methylene chloride. This indicates that when a palladium center is on the surface of the catalyst and unobstructed by aluminum chloride the palladium center will totally hydrodechlorinate the carbon tetrachloride to methane and sub-hydrocarbon species which may oligomerize to form larger chain hydrocarbon products via a Fisher-Tropsch type mechanism. These results are consistant with what has been reported in the literature for palladium based dehydrochlorination and hydrodechlorination catalysts.[74-81] When the palladium

center is obstructed by aluminum chloride on the surface (method I) the carbon tetrachloride cannot directly interact with the palladium center which will leave the palladium center free to activate dihydrogen to form palladium hydrides. The carbon tetrachloride interacts with the acidic chloroaluminum species on the catalyst surface and using a hydride from the palladium center (hydrogen spillover) exchanges a single chloride for a hydride, forming chloroform.

The next catalyst used was a K_2PdCl_4-doped acid catalyst prepared by method I. This catalyst was chosen because no $Pd(II)Cl_2$ was available at the time and it was thought that by starting with a different Pd(II) species might give valuable information on the role of the metal oxidation state and to determine what the effect the potassium ions would have on the catalysts performance. The catalyst was reacted with carbon tetrachloride at 100°C with the carbon tetrachloride pulses at a 30 minute addition rate. The catalyst was very active for the production of hydrocarbons with methane by far the major product. This is a surprising result since it was believed that if the palladium center was covered by aluminum chloride the activity of the catalyst for total hydrodechlorination of carbon tetrachloride would be diminished. There are at least two possible explanations for the catalysts behavior. The first is that the K_2PdCl_4 moiety used is not totally covered by the aluminum chloride due to its large size compared to $Pd(II)Cl_2$ and results in the palladium centers ability to interact directly with the carbon

tetrachloride. Another explanation is that the K_2PdCl_4 starting material reacted with the aluminum chloride to form $AlCl_4^-$ species on the silica gel surface. This would tie up the K_2PdCl_4 as an aluminum chloride complex.

Shown in Figure 3-2 is the product distributions and catalyst activities for the reaction of $Pd(II)Cl_2$-doped acid catalyst (method II), $K_2Pd(II)Cl_4$-doped acid catalyst (method I), and Pd-on-alumina with carbon tetrachloride and hydrogen at 100°C in a syringe pumped flow reactor. The product selectivity for each of the catalysts is the same and the only difference is the activities for each product. It is worthy to note that the $K_2Pd(II)Cl_4$-doped acid catalyst is the least active which suggests that the potassium ions decrease the catalysts ability to effectively interact with carbon tetrachloride and hence hydrodechlorinate to form hydrocarbon products.

The next set of experiments conducted involve the use of 1,2-dichloroethane as a reactant. The first experiment involving 1,2-dichloroethane consisted of taking the K_2PdCl_4-doped acid catalyst and (after purging for 24 hours) adding 1,2-dichloroethane at 100°C. From this reaction ethane and ethyl chloride were observed as products along with some methane and propane which was from some of the carbon tetrachloride still left in the reactor. When the reaction temperature was raised to 125°C and 150°C the catalyst activity increased for all products. At 150°C a trace amount of what appeared to be vinyl chloride was detected. This

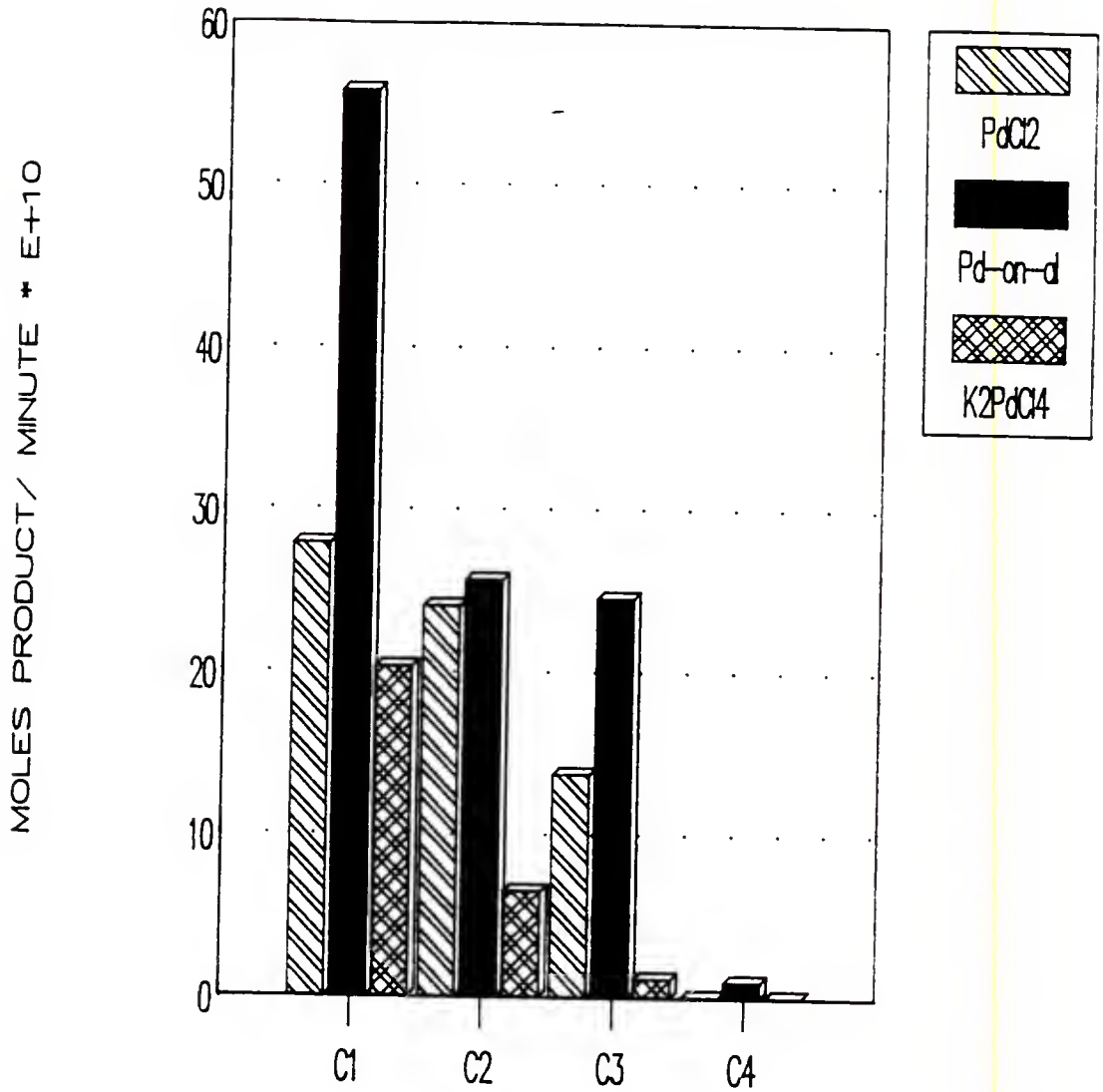


Figure 3-2. Comparison of the Product Distributions for the Reaction of Various Catalysts with CCl_4 at 100°C.

experiment was terminated due to the uncertainty of the catalyst condition (used previously for carbon tetrachloride conversion).

With a clean syringe pumped flow system the reaction of 1,2-dichloroethane and hydrogen with a $Pd(II)Cl_2$ doped $AlCl_3/SiO_2$ catalyst at 100°C was conducted. At T= 30 minutes a GC chromatogram of the product stream revealed ethane, ethyl chloride and what appeared to be vinyl chloride as products. The peak which would correspond to vinyl chloride was small and the peaks for ethane and ethyl chloride were large. By T= 390 minutes the catalyst was reaching maximum activity and the three products of the reaction were ethane, ethyl chloride, and vinyl chloride. The amounts of vinyl chloride and ethyl chloride were about equal. The catalyst was run for 3100 minutes at 100°C in which time the effect of flow rate and pulse length were studied. After 3100 minutes the temperature was changed to 80, 100, 125, 150, 175, 150, and 100°C respectively. The results of the experiment are described in the following paragraphs.

Figure 3-3 shows the results of a GC/FTIR experiment on the product stream from the reaction of 1,2-dichloroethane with the $Pd(II)Cl_2$ doped $AlCl_3/SiO_2$ catalyst. The doubling of the first two peaks is caused by the injection technique and the composition of the peaks are identical. As can be seen in Figure 3-3 the reaction is very clean giving three products. Notice that there is a small amount of carbon tetrachloride still in the reactor. The carbon tetrachloride in larger concentrations gives rise to hydrocarbons such as methane, ethane, propane, and chloroform. At

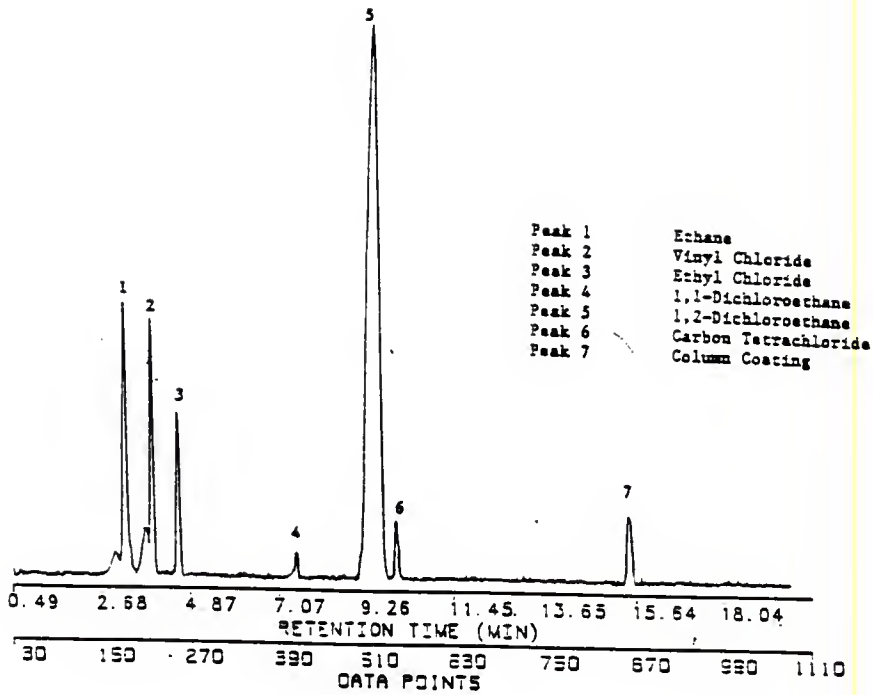

Peak 1 Ethane
Peak 2 Vinyl Chloride
Peak 3 Ethyl Chloride
Peak 4 1,1-Dichloroethane
Peak 5 1,2-Dichloroethane
Peak 6 Carbon Tetrachloride
Peak 7 Column Coating
0.49 2.68 4.87 7.07 9.26 11.45 13.65 15.64 18.04
RETENTION TIME (MIN)
30 150 270 390 510 630 750 870 990 1110
DATA POINTS

Figure 3-3. GC-FTIR Chromatogram of the Product Stream from the Reaction of a $Pd(II)Cl_2AlCl_2$-SiO_2 Catalyst with 1,2-Dichloroethane at 175°C.

low concentrations of carbon tetrachloride these products are not detectable. When hydrocarbons were detected theywere in trace amounts.

Evidence for vinyl chloride production was obtained by GC/FTIR, GC/MS, and GC retention time. The IR for Peak #2 in Figure 3-3 is shown in Figure 3-4 along with the 4 best EPA Vapor Phase Library matches (vinyl chloride was the best pick).

The results of the difference in flow rate (Figure 3-5) indicates that at fast flow rates, ethane production is favored over vinyl chloride or ethyl chloride. If the 1,2-dichloroethane addition period is extended from 30 to 60 minutes (Figure 3-6) a slight increase in activity is observed but, product ratios remain approximately the same.

Figure 3-7 represents the product distribution and catalyst activity at various temperatures. Preliminary results suggest that two reaction temperature regions are favorable for the formation of vinyl chloride and ethyl chloride. The higher temperature however, results in higher ethane production which is undesirable.

Several other metal doped acid catalyst were tried for the hydrodechlorination of carbon tetrachloride. Two metals which have been tried are iron and cobalt. The iron used was in the form of iron(III) chloride and the cobalt was in the form of cobalt(II) chloride. Both catalysts were prepared by method I. The cobalt catalyst generated only small amounts of methane and the iron

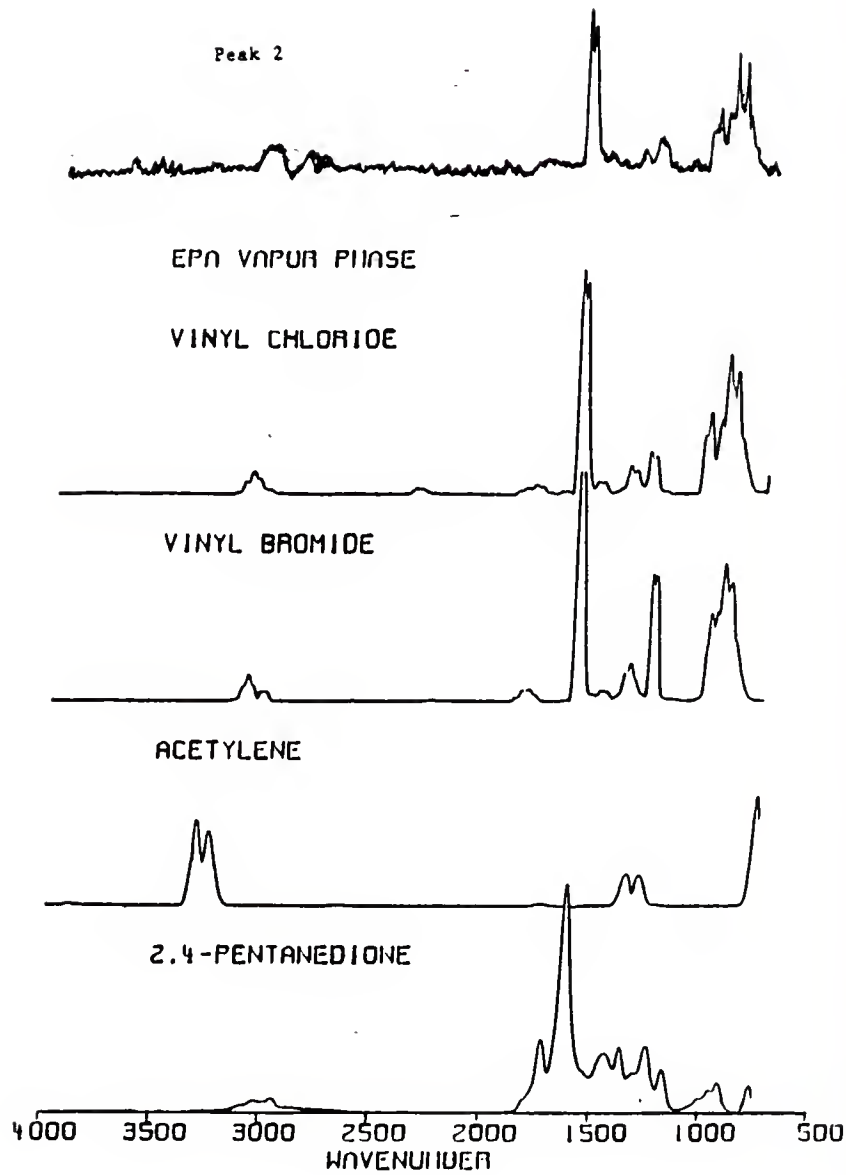


Figure 3-4. Infrared Spectrum of Vinyl Chloride with EPA Vapor Phase Library Best Matches.

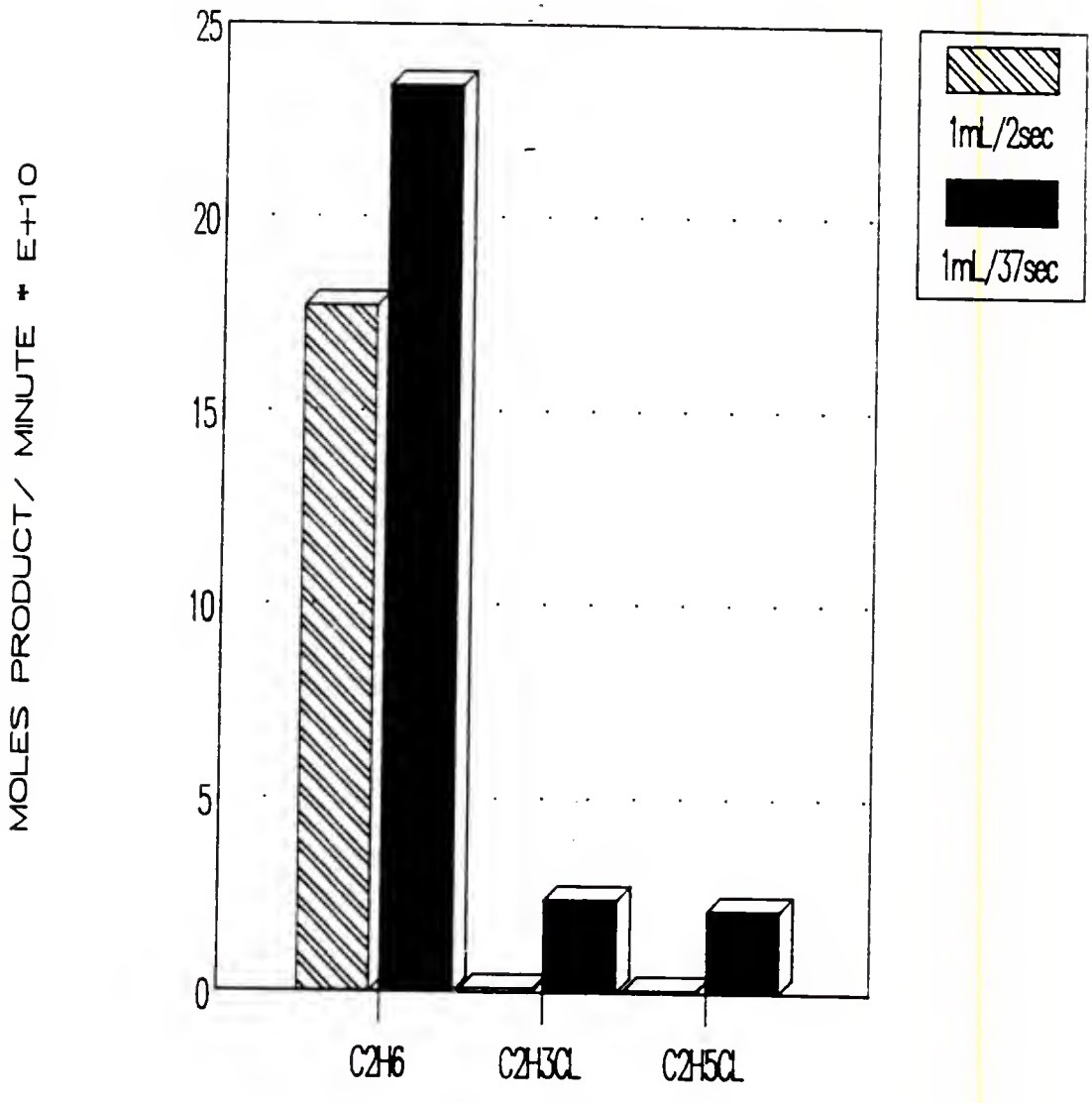


Figure 3-5. Product Distribution from the Reaction of 1,2-Dichloroethane with $Pd(II)Cl_2AlCl_2$-SiO_2 Catalyst at 100°C and a Flow Rate of 1mL/2.4 sec.

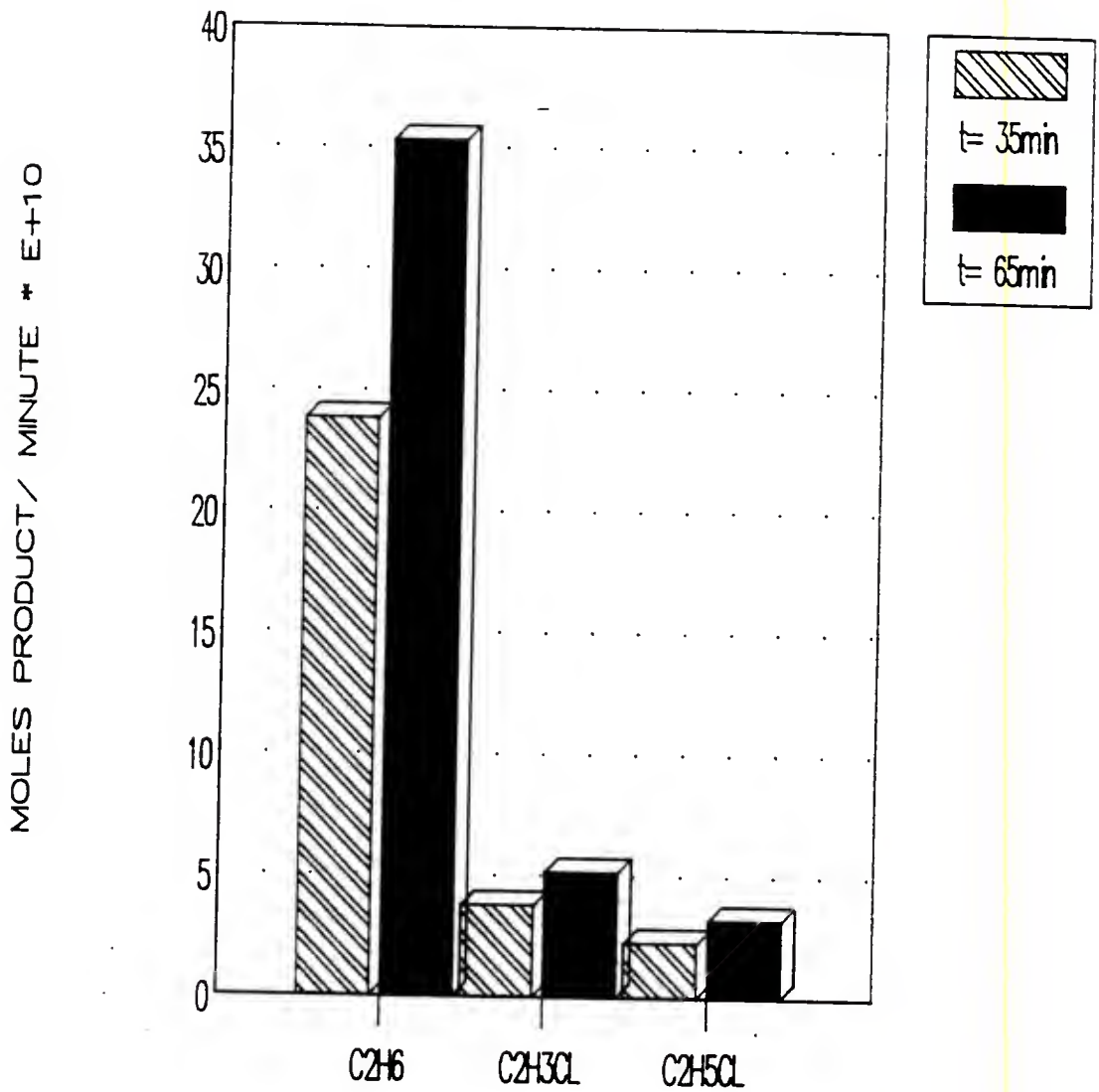


Figure 3-6. Product Distribution from the Reaction of 1,2-Dichloroethane with $Pd(II)Cl_2AlCl_2$-SiO_2 (Type II) Catalyst at 100°C and Various Addition Times.

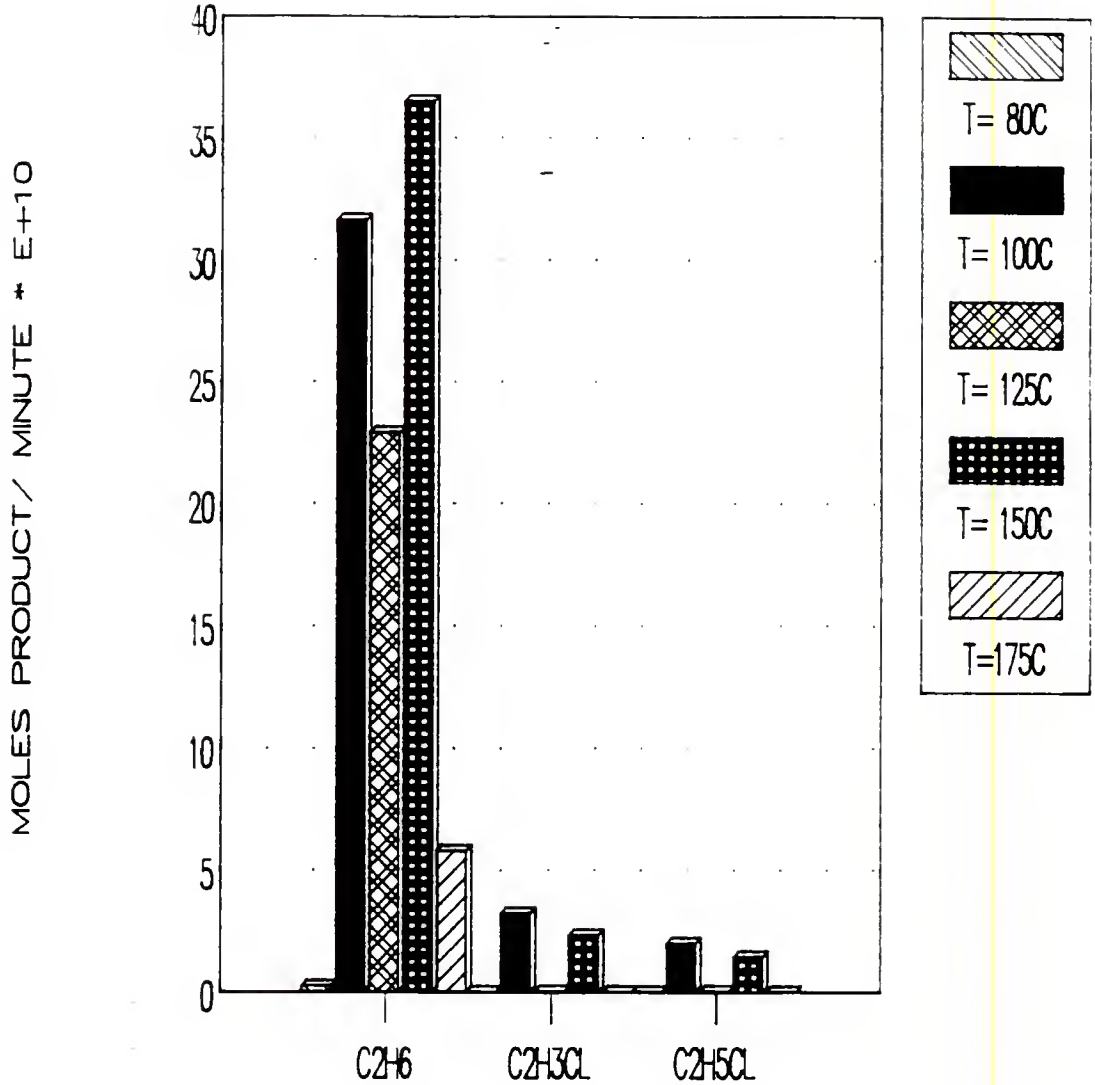


Figure 3-7. Product Distribution from the Reaction of 1,2-Dichloroethane with $Pd(II)Cl_2AlCl_2$-SiO_2 (Type II) Catalyst at Various Temperatures.

catalyst generated traces of hydrocarbons and small amounts of $CHCl_3$. Both were considered inactive.

In continuing the line of experiments performed for the reaction of C-Cl bonds, transition metal-doped catalysts were employed for the dehydrochlorination of 1,2-dichloroethane. The metals used for the latest experiments were rhodium, ruthenium and palladium as well as the undoped acid catalyst.

Results for the $Rh(III)Cl_3AlCl_2$-SiO_2 catalyst are shown in Figure 3-8. This rhodium catalyst was prepared by the reaction of $RhCl_3$ and SiO_2 in carbon tetrachloride at reflux temperature, isolation of the $Rh(III)Cl_3$-SiO_2 solid and subsequent reaction of the $Rh(III)Cl_3$-SiO_2 solid with aluminum chloride at reflux.

At all temperatures studied ethane was by far the most abundant product with only trace quantities of vinyl chloride being detected. The $RhCl_3$ catalyst would seem to be performing the hydrodechlorination reaction very efficiently with only a small amount of dehydrochlorination occurring. An alternative route would be a very facile dehydrochlorination of 1,2-dichloroethane to ethylene and subsequent hydrogenation of the ethylene to ethane. The former explanation seems to be more valid since little vinyl chloride is observed in the product stream. In either case no carbon-carbon bond cleavage products are observed using this catalyst.

The next catalyst studied was a $Ru(III)Cl_3AlCl_2$-SiO_2 catalyst prepared by refluxing $RuCl_3$ and silica gel in carbon tetrachloride

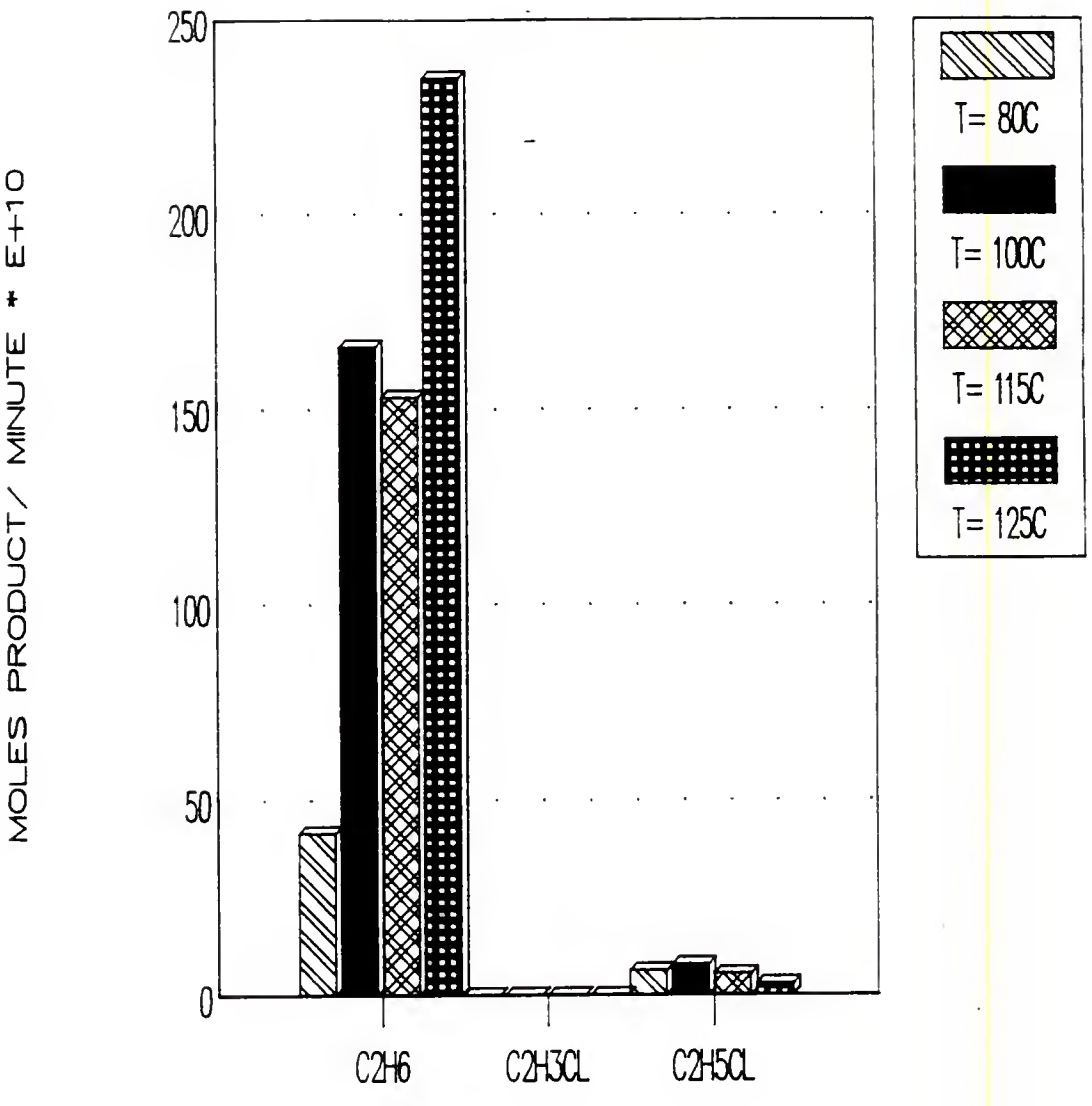


Figure 3-8. Product Distribution from the Reaction of 1,2-Dichloroethane with $Rh(III)Cl_3AlCl_2$-SiO_2 Catalyst at Various Temperatures.

and after several hours the aluminum chloride was added to the reaction mixture to form the final catalyst.

Of all the catalysts studied to date the $RuCl_3$ catalyst is by far the most selective catalyst for the production of vinyl chloride. The catalyst showed good resistance to coking and was stable at reaction temperatures of up to 200°C. The results of the ruthenium doped acid catalyst are shown in Figure 3-9.

The commercial dehydrochlorination of 1,2-dichloroethane is performed at 450°C-550°C under a pressure of 4 MPa.[72] Many by-products are formed from the reaction and to decrease the amount of by-product formation the conversion level of 1,2-dichloroethane to vinyl chloride is maintained at 50-60%. A selectivity of 95-98% to vinyl chloride can be achieved under these reaction conditions. It should be noted that the ruthenium chloride based catalyst operates at much lower pressures and temperatures.

Figures 3-10 to 3-14 are summaries of the other catalysts tried for the dehydrochlorination of 1,2-dichloroethane. The $K_2PdCl_4AlCl_2$-SiO_2 catalyst in Figure 3-10 was prepared by method I without isolation of the metal-doped silica gel solid. The temperature range studied was from 100 to 215°C. Results from this catalyst are similar to that of the $RhCl_3$-doped catalyst in that only trace quantities or no vinyl chloride was detected in the product stream. At a temperature of 200°C the conversion of 1,2-dichloroethane was at a maximum.

The next catalyst used for the dehydrochlorination of 1,2-dichloroethane was an Al_2Cl_6 treated $Pd(II)Cl_2$-SiO_2 catalyst

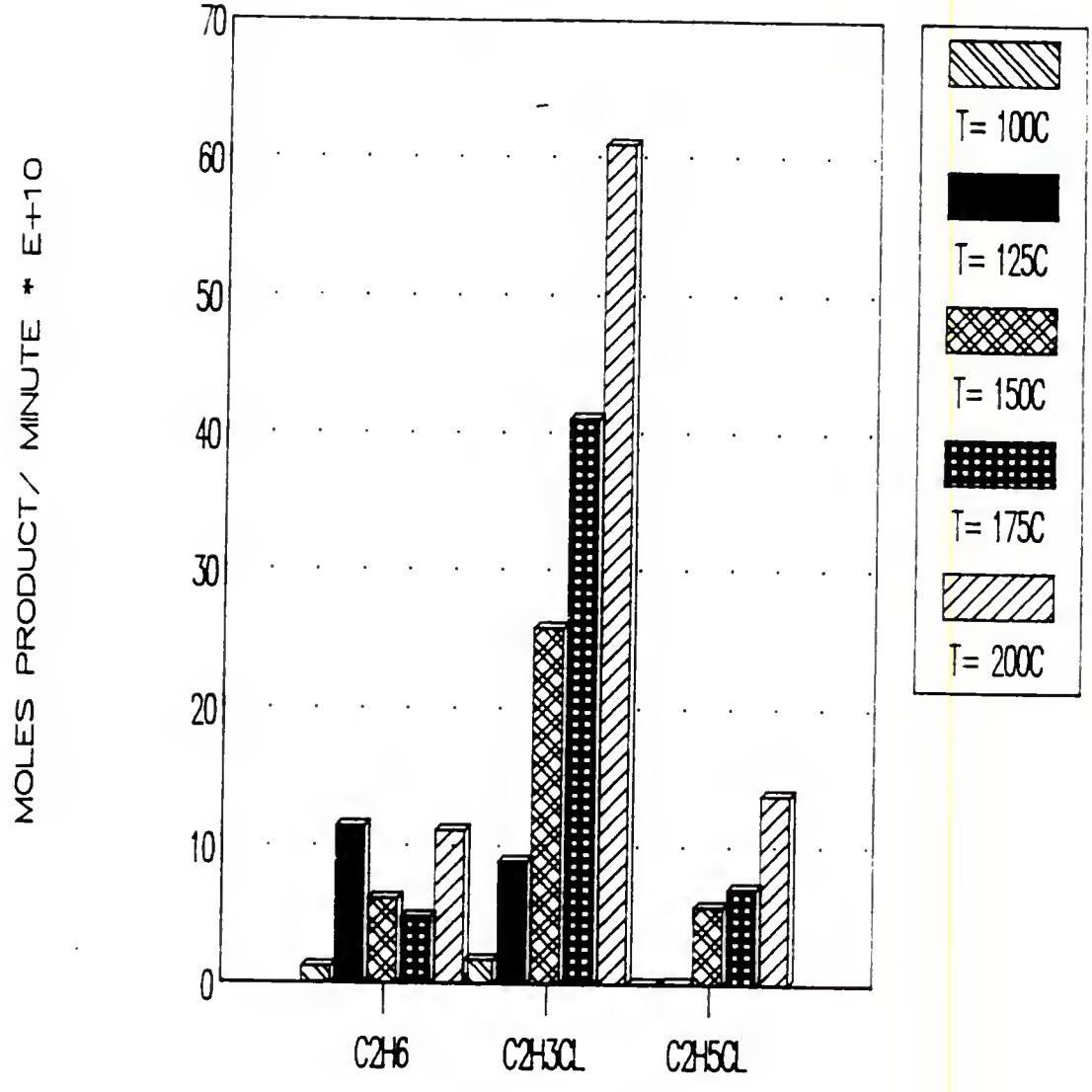


Figure 3-9. Product Distribution from the Reaction of 1,2-Dichloroethane with $Ru(III)Cl_3AlCl_2$-SiO_2 Catalyst at Various Temperatures.

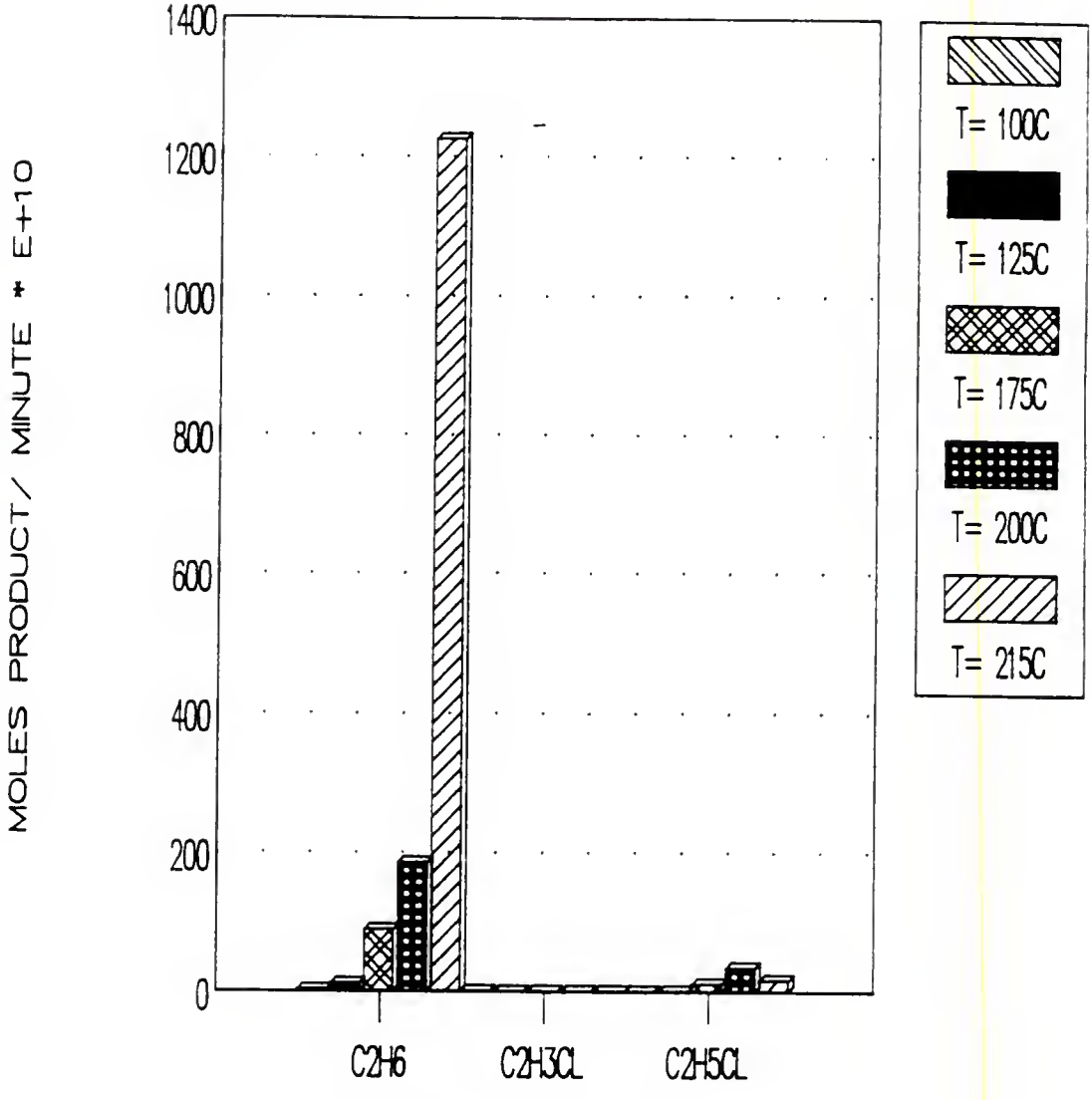


Figure 3-10. Product Distribution from the Reaction of 1,2-Dichloroethane with $K_2Pd(II)Cl_4AlCl_2$-SiO_2 Catalyst at Various Temperatures.

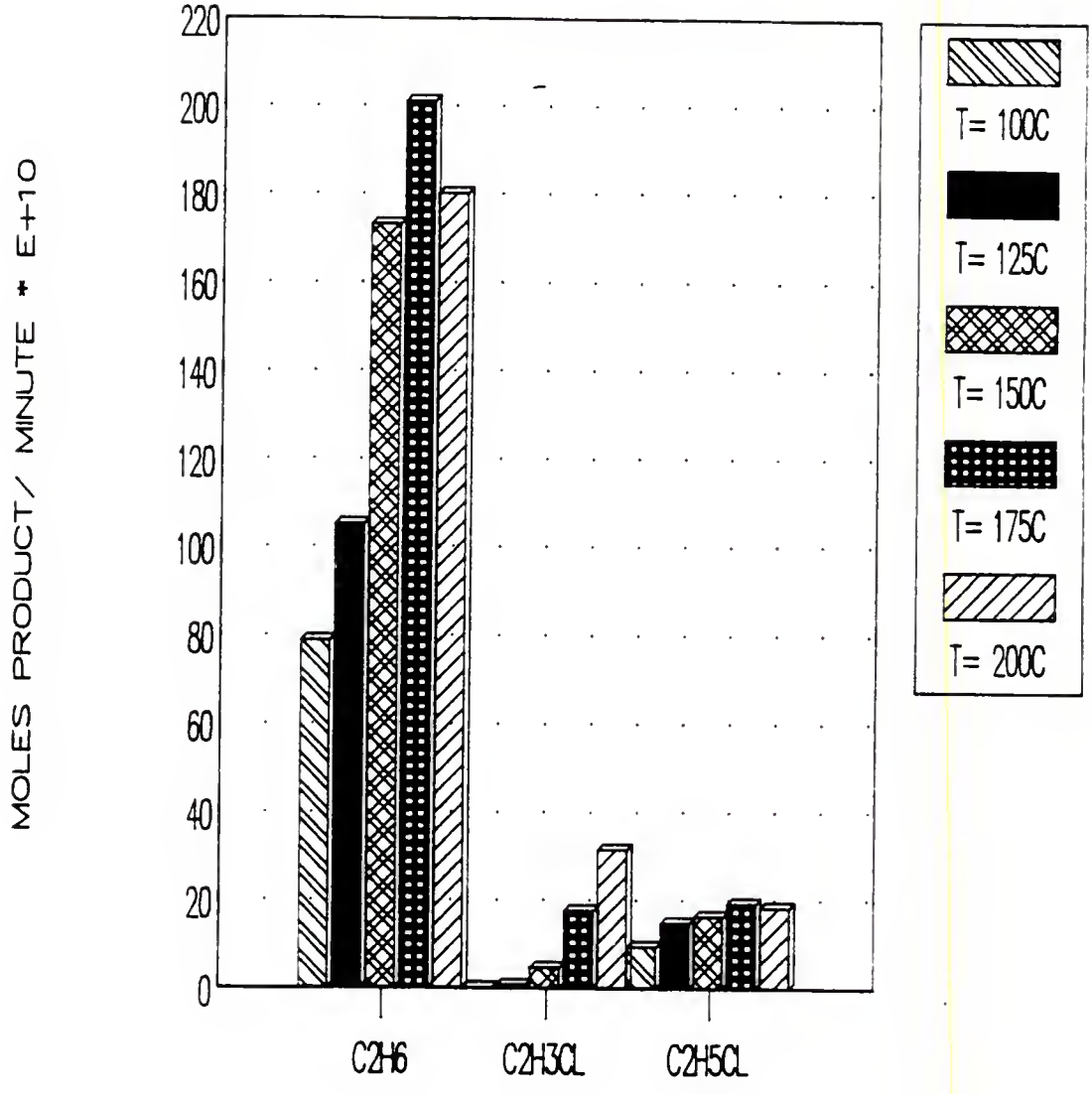


Figure 3-11. Product Distribution from the Reaction of 1,2-Dichloroethane with $Pd(II)Cl_2AlCl_2$-SiO_2 (Type I) Catalyst at Various Temperatures.

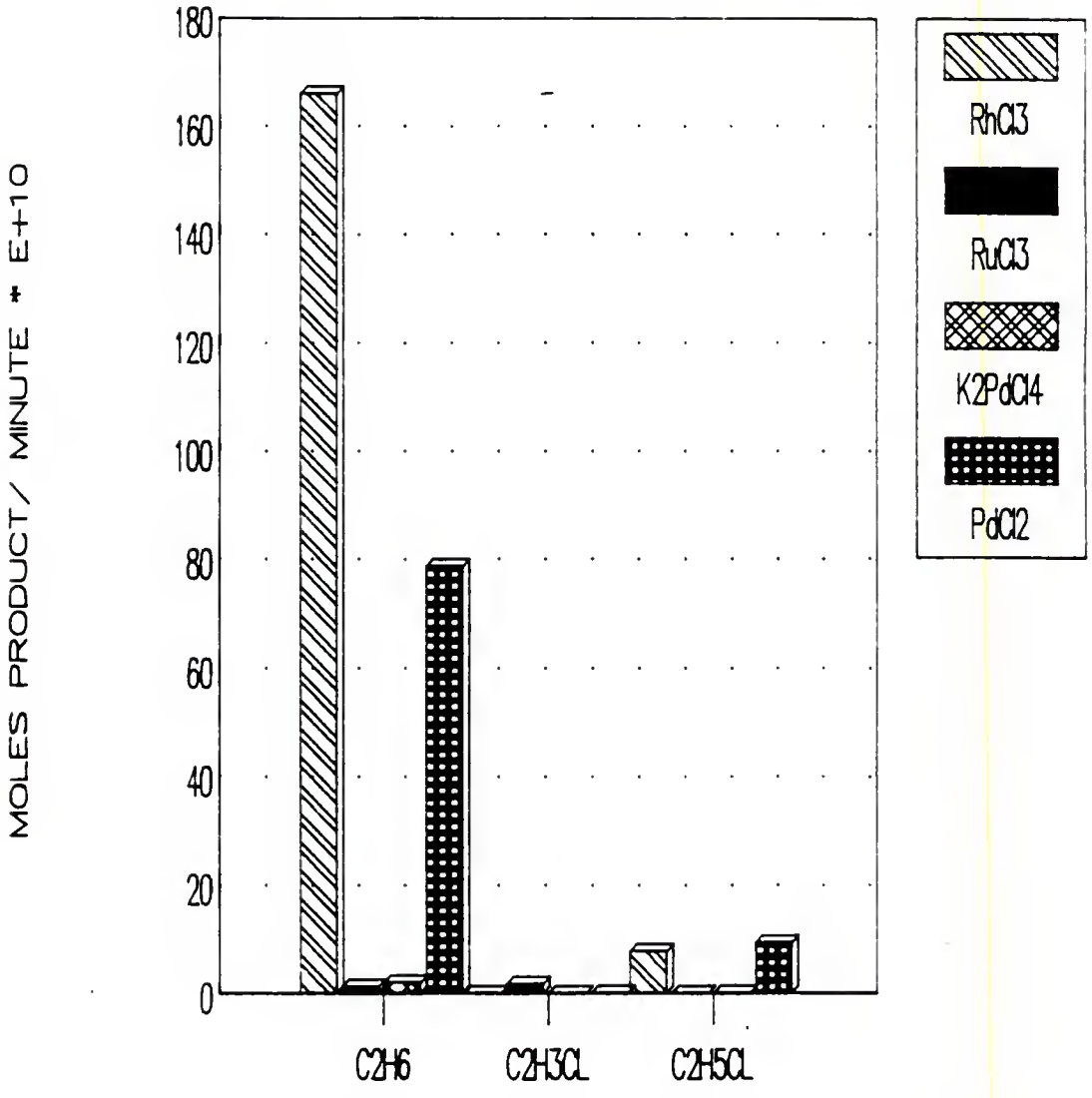


Figure 3-12. Comparison of all Catalysts Reacted with 1,2-Dichloroethane at 100°C.

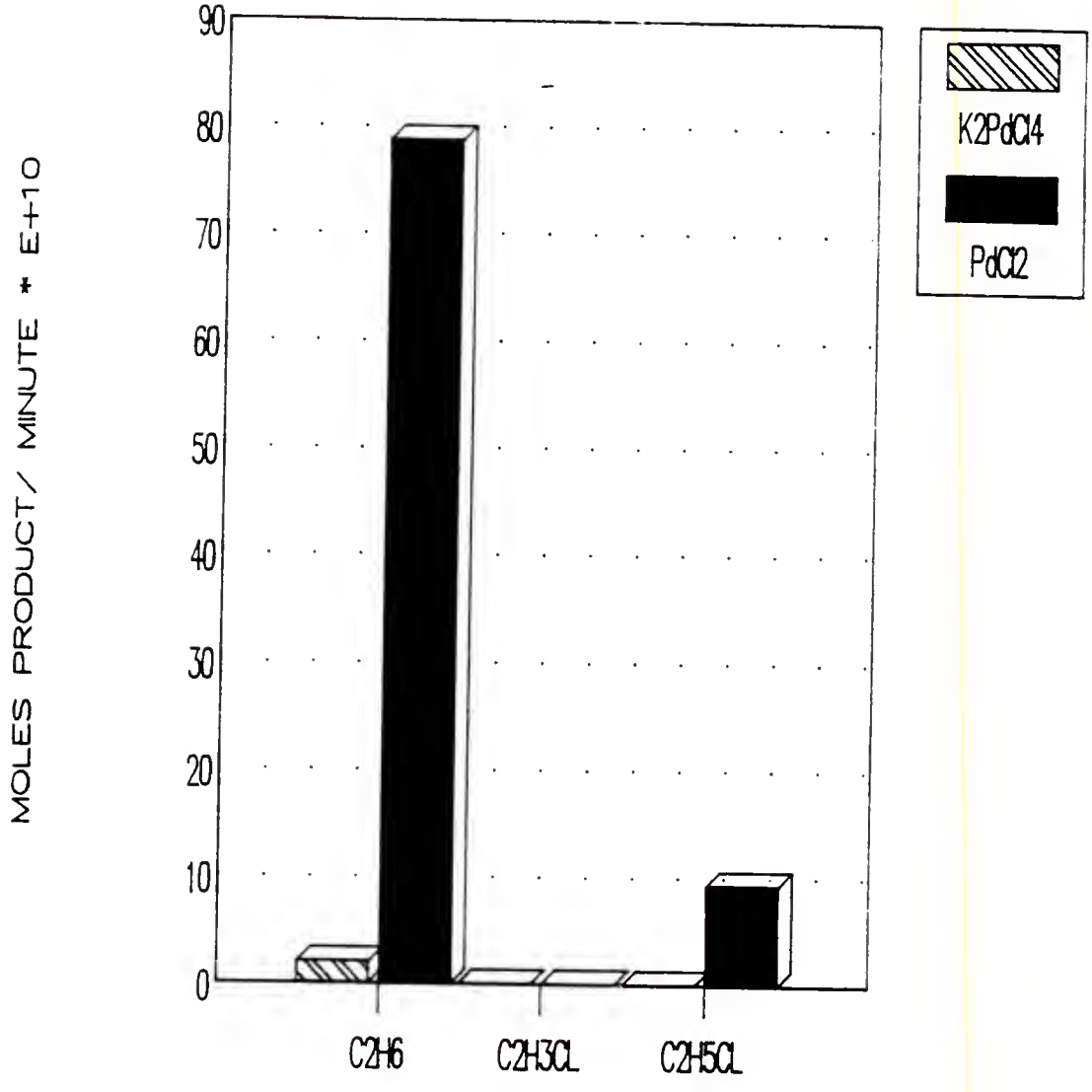


Figure 3-13. Comparison of the $PdCl_2$ and K_2PdCl_4 Doped Solid Acid Catalysts (Type I).

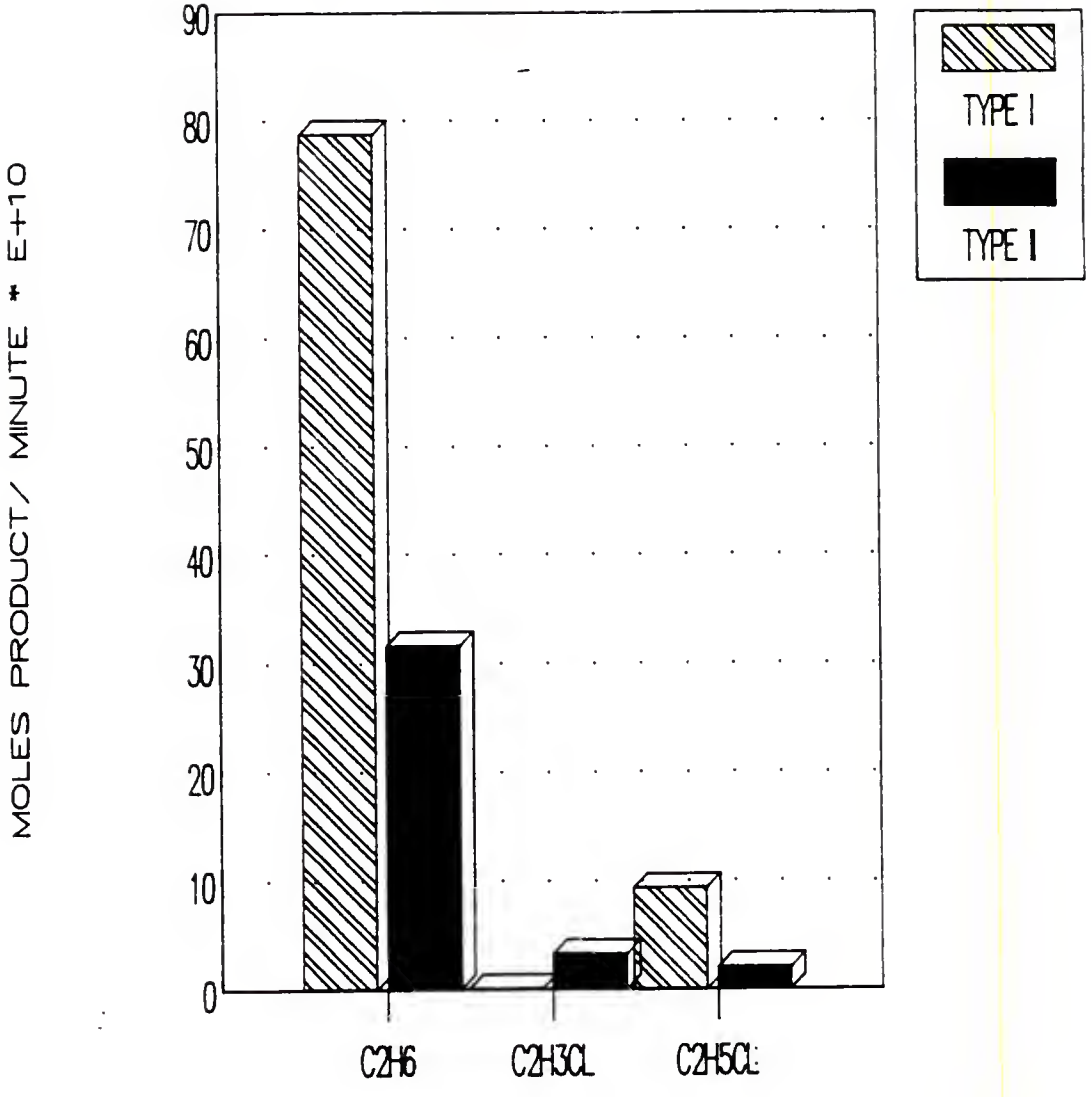


Figure 3-14. Comparison of the $PdCl_2$ Doped Acid Catalysts Prepared by Method I and Method II.

The $PdCl_2AlCl_2$-SiO_2 catalyst was effective for the conversion of 1,2-dichloroethane to vinyl chloride. Maximum conversion of 1,2-dichloroethane was observed at 200°C with a subsequent decrease in ethane production which had a maximum at 175°C. Results for the $Pd(II)Cl_2$ catalyst are shown in Figure 3-11.

When all of the metal-doped catalyst (prepared by method I) activities are compared (for the reaction with 1,2-dichloroethane at 100°C) it is observed that the $RhCl_3$ and $PdCl_2$ catalysts are the most active in terms of overall activity (Figure 3-12).

Figures 3-13 and 3-14 show the comparisons of the $PdCl_2$ and K_2PdCl_4-SiO_2 catalysts and the Al_2Cl_6 treated $Pd(II)Cl_2$-SiO_2 and the $Pd(II)Cl_2$ doped $AlCl_3/SiO_2$ catalysts, respectively. Of all these catalysts only the $PdCl_2$ Type II catalyst was effective for the dehydrochlorination of 1,2-dichloroethane to vinyl chloride at 100°C.

As a blank reaction the undoped acid catalyst was used for the dehydrochlorination of 1,2-dichloroethane. The reaction of $AlCl_2$-SiO_2 with 1,2-dichloroethane was conducted at temperatures of 100 to 175°C. At all temperatures little or no vinyl chloride was observed. The undoped catalyst also showed signs of extreme coking. Two products were produced during the reaction which were of importance. One product was ethyl chloride and the other was 1,1-dichloroethane. Figure 3-15 shows the activity of the undoped catalyst at various temperatures for ethyl chloride. Notice that the undoped catalyst is much less active than any of the metal-doped catalysts used. The conversion of 1,2-dichloroethane to

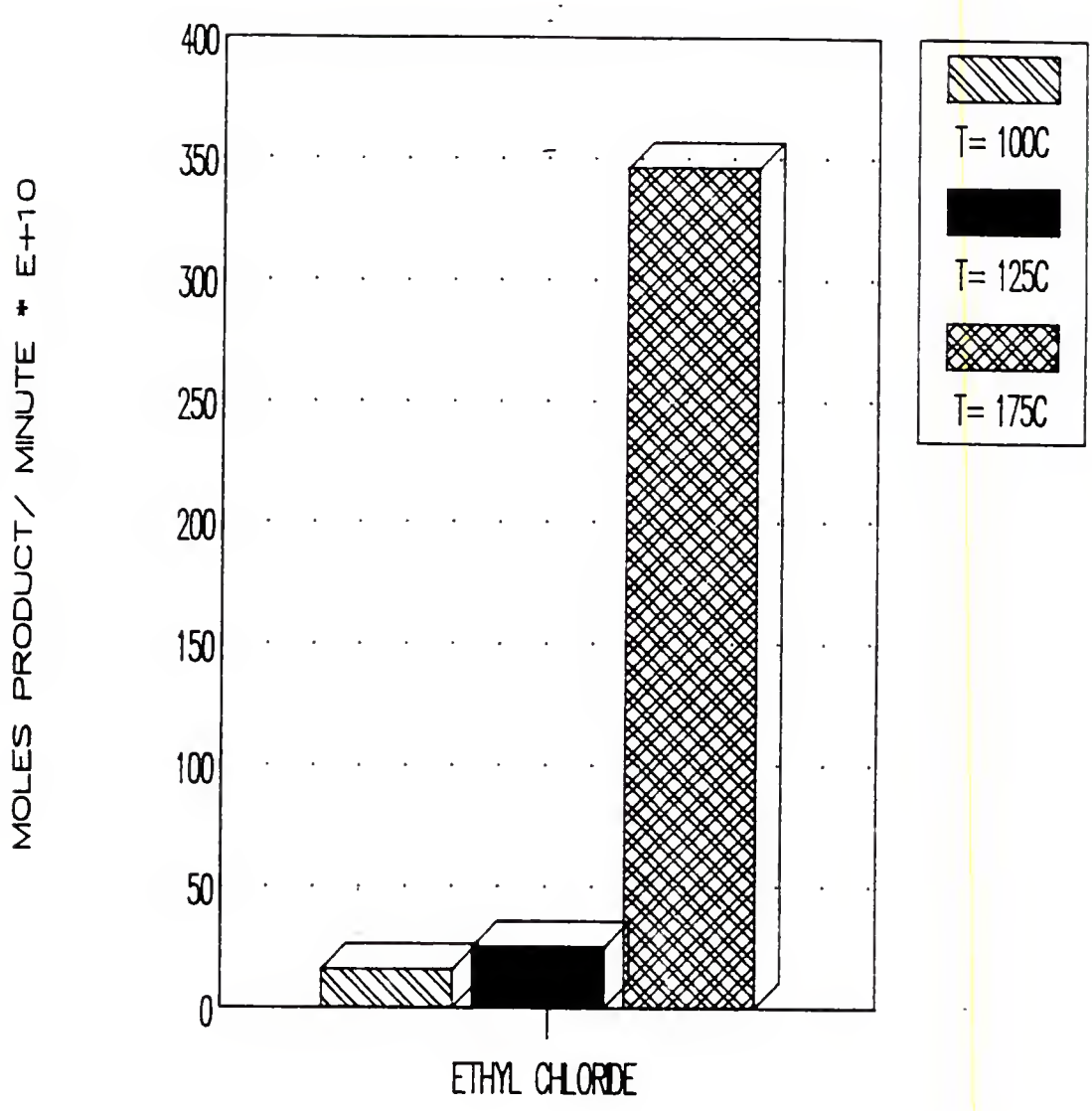


Figure 3-15. Product Distribution for the Reaction of 1,2-Dichloroethane with $AlCl_2$-SiO_2 catalyst at Various Reaction Temperatures.

1,1-dichloroethane was the predominant reaction and at 175°C the conversion was estimated at 48.5%. The production of 1,1-dichloroethane from 1,2-dichloroethane was only observed for the undoped acid catalyst.

Hydrodechlorination of Carbon Tetrachloride at High Conversion Rates

The work reported in this section employs the use of a modified syringe pumped flow reactor with higher space velocities and shorter retention times. The modifications to the flow system includes the use of a preheated zone which is ten times thecatalyst zone. This allows proper mixing and heating of the reactants before they come into contact with the catalyst. Another modification employs the use of a rotaflow meter to monitor the hydrogen gas flow through the system. Typical reaction conditions were used with flow rates of 180 cc/min to 360 cc/min and 0.01 cc/min of carbon tetrachloride at temperatures of 100°C to 200°C. Hydrogen chloride evolution was monitored by dispersion of effluent gas through dH_2O and titration of the HCl/dH_2O solution with a standardized NaOH solution. The catalysts used were the $RhCl_3$, $RuCl_3$, $PdCl_2$ and $CuCl_2/RhCl_3$ doped acid catalysts prepared by method I. Collection times for the detection of HCl were from 30 to 60 minutes. Products were detected by GC using FID for the hydrocarbon products and TCD for the detection of the chlorinated hydrocarbon products. Mass balances were performed on the reactions however the hydrogen in the effluent gas stream was not quantified so the mass balance for hydrogen did not equal 100%.

The mass balance for carbon did not equal 100% in all the runs and was due to other products being formed. One of those products was hexachloroethane. At the end of the $RhCl_3$ catalyst run 0.140g (5.9×10^{-4} moles) of C_2Cl_6 was isolated as white crystals on the walls of the reactor after the catalyst zone. This most likely represents a small portion of the C_2Cl_6 actually formed. The formation of hexachloroethane indicates that a radical mechanism for the hydrodechlorination is occurring which is consistent with what is reported in the literature.[77,81] In all cases greater than 60% of the HCl detected resulted from the production of methane. For the $RhCl_3AlCl_2$-SilicaGel catalyst the maximum conversion rate of carbon tetrachloride to chloroform occurred at a temperature of 150°C. The conversion rate at 150°C was 0.057 grams CCl_4/gram-cat*hour to chloroform (a 1.2% conversion). The maximum conversion rate of carbon tetrachloride to products occurred at 200°C with a rate of 0.43 grams CCl_4/gram-cat*hour (a 96.4% conversion).

The effluent gas was collected for a total of 410.75 minutes (in a reaction temperature range from 100°C to 200°C) which corresponds to 4.12 grams of carbon tetrachloride added. The carbon tetrachloride was converted to 3.34grams of products which is a 81.1% conversion of carbon tetrachloride to products. For the $RuCl_3AlCl_2$-SilicaGel catalyst the maximum conversion rate to chloroform occurred at a temperature of 200°C with a conversion rate of 0.0136 grams CCl_4/gram-cat*hour. The conversion rate of carbon tetrachloride to products at 200°C is 0.0271 grams

CCl_4/gram-cat*hour. The effluent gas was collected for a total of 1162.5 minutes which corresponds to 11.625 grams CCl_4 added. The carbon tetrachloride was converted to 0.371 grams products which is a 3.19% conversion.

One attempt employing a $PdCl_2$-doped catalyst resulted in some chloroform production. At a temperature of 100°C a conversion rate of 0.003 grams CCl_4/gram-cat*hour was observed which is a 0.5% conversion to chloroform. A second trial of the PdCl2$AlCl_2$-SilicaGel catalyst revealed only hydrocarbons as products. The total conversion was greater than 50% but no chloroform was produced. A blank reaction using Pd(II)Cl_2-on-silica gel without aluminum chloride present showed no activity even at 225°C. A new catalyst has been prepared which contains 2% $CuCl_2$ and 0.02% $RhCl_3$-on-silica gel which is then reacted with aluminum chloride. This catalyst showed good production of chloroform with greatly reduced hydrocarbon production at a temperature range between 150°C and 200°C.

This system must be run and quantitative results obtained. The results from our last set of experiments indicated that hydrocarbon formation from carbon tetrachloride is the predominant pathway. This is due to the high concentration of noble metal present on the surface of the catalyst. One way in which to decrease the formation of the hydrocarbons is to use much less noble metal. Currently a 2% loading is used and this amount could be lowered to 0.05% if the function of the metal in forming chloroform is to generate hydride from dihydrogen. In order to

get good dispersion and to make sure the noble metal is not on the catalyst surface the noble metal is deposited with 2% of a metal chloride, oxide or carbonyl which does not react with carbon tetrachloride alone. This support material is then treated with aluminum chloride to produce our final catalyst. In this way it is hoped that the higher dispersion will cause a decrease the catalysts activity for hydrocarbon formation and increase the production of chloroform from carbon tetrachloride. The bulk metal chloride or metal oxide that are currently being studied are $CuCl_2$ and $CoCl_2$. Copper chloride and cobalt chloride were chosen because they show no activity for the reduction of carbon tetrachloride.

A catalyst was prepared that consisted of 0.02% $RuCl_3$/2% $CuCl_2$ on silica gel that was treated with aluminum chloride. When this catalyst was run for the hydrodechlorination of carbon tetrachloride the activity for chloroform production was the same as the 2% $RuCl_3$ doped acid catalyst and the amount of hydrocarbons formed was diminished. This system did not show an increase in chloroform production and still formed hydrocarbon products.

Heterogenous Hydrodechlorination of Carbon Tetrachloride

As eluded to earlier, the noble metal doped solid acid catalysts are too reactive with carbon tetrachloride to produce chloroform selectively without an additional hydrocarbon in the reactant stream. The reaction path toward methane and sub-hydrocarbon species from carbon tetrachloride is very facile and

causes the formation of unwanted hydrocarbons instead of chloroform. The chemistry involved is the radical chemistry of the nobel metals and is well known. It is this radical chemistry that gives rise to the unselective conversion of carbon tetrachloride to hydrocarbons and hence a new reaction system needs to be developed which excludes this type of radical chemistry or operates under less stringent conditions.

One direction that can be taken is to look at more milder hydrogenation systems such as metal carbonyl complexes and organometallic systems. There have been reports in the literature of noble metal carbonyl complexes and organometallic complexes used to activate carbon-chlorine bonds.[84-86] A report by Kono et al.[85] states that hydrogen-chlorine exchange between organo silicon hydrides and polychloro-alkanes can be catalyzed by ruthenium(II)-phosphine complexes. The systems can give 100% conversion of carbon tetrachloride to chloroform however, the systems is stoichiometric in silicon-hydride which makes the process unattractive. A report by Ungvary and Marko[86] states that the stoichiometric hydrodehalogenation and formylation of organic halides may be conducted using tetracarbonyl cobaltate(-I). This reaction proceeds by generation of hydrido tetracarbonyl cobaltate and an alkyl tetracarbonyl cobaltate species which react to form R-H and dicobaltoctacarbonyl.

The use of hydrido cobalt tetracarbonyl as a hydrogenation catalyst has been well documented[87] and is postulated as the catalytic species in the cobalt catalyzed hydroformylation of

olefins using dicobalt octacarbonyl.[88] In examining the mechanism for the hydrodechlorination of carbon tetrachloride using dicobalt octacarbonyl a similarity between the hydrodechlorination and hydroformylation reaction is observed. Both reactions involve the formation of hydrido cobalt tetracarbonyl and activation of the substrate by oxidative addition to form an alkyl cobalt tetracarbonyl complex which will then react with cobalt hydride to reductively eliminate an alkane and form dicobalt octacarbonyl. Indeed, it was reported by Ungvary and Marko[86] that the Cl_3C-Co(CO)4 complex would insert carbon monoxide to form the acyl-cobalt complex which then will react with hydrido cobalt tetracarbonyl to form the formylated products. It has been stated in a review of the activation of molecular hydrogen[83] that the activation of alkyl and acyl halides by platinum group metal complexes is closely related to the activation of hydrogen.

With this information in mind a new set of a catalysts were employed for the conversion of carbon tetrachloride into chloroform. Several catalysts were prepared which contained two group VIII-metal carbonyl clusters bound to a silica support through diphenylphosphino silane linkages. The method of anchoring metal carbonyl clusters to supports via organo silanes is well known and has been reported extensively in the literature.[89-91] These heterogenous metal carbonyl catalysts were used in order to have milder hydrogenation systems than the metal or metal chloride systems previously tried.

The first catalyst used was a silica gel supported $Rh_6(CO)_{16}$ /$Co_2(CO)_8$ system using an organosilane linkage to the support. The total loading of metal carbonyl was 0.5 mmole/gram with a $Rh_6(CO)_{16}$ to $Co_2(CO)_8$ ratio of 1:1. One gram of catalyst was used in the syringe pumped flow reactor with an addition rate of CCl4 of 0.01 cc/min, a hydrogen flow rate of 120 to 190 cc/min and a temperature range of 90 - 200°C. At 90 °C the conversion of carbon tetrachloride to chloroform was 0.00062% and the total conversion of carbon tetrachloride to products was 0.06%. Products observed other than chloroform were C_1-C_3 hydrocarbons. As the temperature was increased from 90°C to 200°C the percent conversion of carbon tetrachloride to chloroform increased from 0.0062 to 3.18% and the total conversion of carbon tetrachloride to products increased from 0.06% to 8.17%. The amount of hydrocarbons produced by this system was significantly lower than the previously studied metal and metal chloride based catalysts. However, the amount of chloroform was not substantially increased. The object in using this system was to have the cobalt carbonyl species react with carbon tetrachloride to form the trichlorocarbon cobalt carbonyl species which could then react with a metal-hydride to form chloroform without hydrocarbon side products. This objective was partially met in that chloroform was produced in significant amounts with a large suppression in hydrocarbon formation. To trace the hydrocarbon formation a $Rh_6(CO)_{16}$ catalyst was used to determine if the hydrocarbons were coming from the rhodium centers. Under the same conditions as the

last catalyst one gram of silica gel supported $Rh_6(CO)_{16}$ using an organo-silane linkage was used at a temperature range of 90 to 200°C. The conversion of the $Rh_6(CO)_{16}$ based catalyst to chloroform at 200°C was 2.07% however a large amount of hexachloroethane was also produced. When the temperature was raised to 225°C the catalyst activity for chloroform dropped to near zero and the amount of carbon tetrachloride in the product stream fell to near zero. Large amounts of hexachloroethane were observed to deposit on the reaction walls and the catalyst turned brown in color. Other metal carbonyls were also used such as $Ru_3(CO)_2$ in combination with $Rh_6(CO)_{16}$ and $Co_2(CO)_8$ but in each case no greater than 4% conversion to chloroform was observed. The large amount of hexachloroethane in the $Rh_6(CO)_{16}$ system indicates that extensive radical chemistry is occurring. Since it was previously stated that a system was desired which did not proceed by a radical mechanism but by a covalent activation of the C-Cl bond a new system was devised which would capitalize on the chemistry of the $HCo(CO)_4$.

A homogenous cobalt hydrogenation catalyst which is similar to the hydride cobalt tetracarbonyl system is the pentacyanocobaltate(II) hydrogenation catalyst. The pentacyanocobaltate(II) species has been studied extensively and there has been many reports published on its reaction and kinetic properties.[92-95]

Solutions of pentacyanocobaltate(II) can be prepared by the addition of excess cyanide to aqueous, methanol or methanol-

glycerol solutions of cobaltous salts under inert atmosphere conditions and may be isolated as salts of the dimer $[Co_2(CN)_{10}]^{6-}$.[92] The dimer is reported to undergo hydrogenation to form $2[HCo(CN)_5]^{3-}$ which may then be used as a hydrogenation catalyst.[92-95] The dimer is also reported to undergo reaction with organic halides to form $[RCo(CN)_5]^{3-} + [XCo(CN)_5]^{3-}$ and in alkaline solutions of $[HCo(CN)_5]^{3-}$ with $[Co(CN)_5]^{3-}$ present the catalytic reduction of organic halides to R-H takes place.[92] To further explore this chemistry for the conversion of carbon tetrachloride to chloroform several reactions were conducted using pentacyano-cobaltate(II) as a hydrogenation catalyst. Since pentacyano-cobaltate(II) has limited solubility,[92] solutions of pentacyano-cobaltate(II) were prepared in aqueous solutions and phase transfer agents were used to bring the pentacyano-cobaltate(II) into the organic solvents. The catalyst was prepared by dissolving 1.3 grams of $CoCl_2$ $6H_2O$ in 100 mL N_2 degassed dH_2O and adding 2.0g NaCN. To the resulting olive green solution a 10 to 25 mL solution of carbon tetrachloride or methylene chloride containing a phase transfer agent in a concentration three times the cobalt concentrations was added. The two phases were separated by Schlenk techniques and placed into a 250 mL pressure bottle equipped with a liquid withdrawal port. A typical experiment employed 50mL of reactant solution containing ~3 x 10^{-3} moles pentacyanocobaltate(II), 9 x 10^{-3} moles phase transfer agent and 30 psig hydrogen with a reaction temperature of 70 to 100°C.

The first reaction conducted used a two solvent system containing carbon tetrachloride and methylene chloride. The reaction was conducted in a 250 mL Parr pressure bottle apparatus which contained 50 mL of a CH_2Cl_2/CCl_4 solution in a 3:1 ratio by volume. The solution contained 1 x 10^{-3} moles of pentacyanocobaltate(II) and 3 x 10^{-3} moles of Benzyldimethylstearyl ammonium chloride monohydrate (phase transfer agent). The apparatus was pressurized with 30 psig H2 and allowed to react mixture turned to an emerald green color from an orange color. From injections before and after catalysis there was a decrease in the amount of methylene chloride by 15.9% and a decrease in the amount of carbon tetrachloride by 8.5%. A two solvent system was used because the phase transfer agent had a limited solubility in carbon tetrachloride. Since the reaction was successful a single chloroform solvent system (CCl_4) was used with a different phase transfer agent in order to study the reaction of carbon tetrachloride more closely.

The next experiment used 50 mL carbon tetrachloride which contained 6 x 10^{-3} moles of Aliquat 336 (Phase transfer agent) to transfer 3.4 x 10^{-3} moles of pentacyanocobaltate(II) out of a dH20 solution. The reaction was run at 100°C and 32 psig H_2. The pressure bottle was repeatedly refilled (purged) with H_2 and samples taken. After 900 minutes however the solution only contained 10.4 mmoles chloroform. The solution was a very dark emerald green in color. If the solution was taken (after T= 975 minutes) and $NaBH_4$ was added, the solution would lighten in color

and chloroform would be produced. If 25 mL of the same solution before catalysis was used with 25 mL dH_2O and 30 psig H_2 at 100°C only 1 mmole of product is observed and the solution remained the original orange color of the carbon tetrachloride solution. Since the original dH_2O solution is olive green (pentacyano-cobaltate(II)) and addition to CCl4 solution produces a solution with an orange-yellow color a reaction must take place. During catalysis in the absence of water, the solution turns an emerald green and chloroform is produced in catalytic quantities. When water is present only stoichiometric quantities are formed and the solution remains the same color. It maybe that in the presence of excess chlorocarbon very little $[HCo(CN)_5]^{3-}$ is formed and the reaction is slow due to the formation of large quantities of chloroalkyl cobalt species. This is indicated by the fact that if a hydride source such as $NaBH_4$ is added, chloroform is produced. In order to overcome the problem associated with neat substrate a co-solvent system was tried where one of the solvents is not a chlorocarbon. The solvent chosen was 1-methyl-2-pyrrolidinone because of its miscibility with carbon tetrachloride and low vapor pressure.

A solution of 1-methyl-2-pyrrolidinone (35 mL) and carbon tetrachloride (15 mL) containing 2.94×10^{-3} moles of cobalt was placed in a Parr pressure bottle apparatus with 32 psig H_2 and heated to 100°C. At T= 60 minutes (1.95 mmole) of $CHCl_3$ were produced at rate of 4 Turnovers per hour. At T= 80 minutes, 14.35 mmoles $CHCl_3$ were produced at a rate of 15.4 Turnover per hour.

At T= 120 the solution was a very dark red color and had an amine odor (pyridine) indicating that decomposition of the solvent was occurring. The HCl generated in the reaction was opening the ring of the 1-methyl-2-pyrrolidinone and the ring opened product was reacting with carbon tetrachloride. The red color may also be due to some polymeric species generated by the reaction with CCl_4.

The biphasic systems studied (CCl_4/dH_2O, CCl_4/ethylene glycol, CCl_4/acetonitrile) give rise to stoichiometric or slightly higher than catalytic amounts of $CHCl_3$. Systems employing pure halogenated solvents such as CCl_4 are catalytic but the rates are extremely low. With this information in mind more emphasis will be placed on finding a miscible co-solvent system for the conversion of CCl_4 to $CHCl_3$. The system of CCl_4/1-methyl-2-pyrrolidinone may be a good system, however, it would have to be run in a stirred-flow batch reactor so that the HCl and $CHCl_3$ generated in the reaction can be removed from the reactor to prevent any solvent decomposition.

3.4 Summary

The main goal of this investigation was to develop a heterogeneous catalyst for the dehydrochlorination and hydrodechlorination of various polychlorinated molecules. Carbon tetrachloride was chosen as a subtrate due to the interest in selectivly converting carbon tetrachloride to chloroform. The other substrate chosen was 1,2-dichloroethane in an attempt to

develop a catalytic process for the production of vinyl chloride. When metal chloride-doped solid acid catalysts were used for the catalytic cracking of hydrocarbons using carbon tetrachloride or tetrachloroethane as a chlorine source, products were observed which correspond to the replacement of a carbon-chlorine bond. One of the first metals chosen was palladium because of its ability to activate dihydrogen. Results from the reaction of the $Pd(II)Cl_2AlCl_2$-silica gel catalyst with CCl_4 and H_2 indicated that the activity and selectivity greatly depended upon the catalyst preparation. When the metal chloride was placed on the inorganic oxide before treatment with aluminum chloride (method I), chloroform was detected in the product stream. Only hydrocarbons were detected in the product stream when the metal chloride was placed on the catalyst after aluminum chloride treatment (method II). The catalyst prepared by method II exhibited properties similar to conventional hydrodechlorination catalysts such as Pd-on-carbon and Pd-on-alumina. When the form of the palladium chloride was changed to the potassium salt (K_2PdCl_4) the activity of the catalyst was decreased and the selectivity remained unchanged. This suggests that the potassium ions reduce the catalysts ability to effectivly interact with the carbon tetrachloride.

Several other metal-doped catalysts were investigated for the hydrodechlorination of carbon tetrachloride. When $CuCl_2$, $CoCl_2$ and $FeCl_3$ were used as the metal chloride no conversion of carbon tetrachloride was evident. For the $RhCl_3$, $RuCl_3$ and $RhCl_3/CuCl_2$

doped catalysts products were detected which corresponded to the hydrodechlorination of CCl_4. In all cases greater than 90% of the products produced was methane.

In addition to the hydrodechlorination of carbon tetrachloride each of the previously mentioned catalysts were used for the dehydrochloriation of 1,2-dichloroethane. The most active catalyst for the conversion of 1,2-dichloroethane to products was the $RhCl_3$-doped acid catalyst. The major product of the reaction was ethane and only trace quantities of vinyl chloride were detected. Once again catalyst activity depended on the catalyst preparation. The $PdCl_2$-doped acid catalyst (method II) was the least active catalyst and the $PdCl_2$-doped acid catalyst (method I) was the second most active catalyst. One catalyst was very selective for the dehydrochlorination of 1,2-dichloroethane to vinyl chloride. The $RuCl_3$-doped acid catalyst at 200°C produced vinyl chloride with an 85% selectivty and moderate activity.

Several heterogeneous metal carbonyl catalysts were investigated for the hydrodechlorination of CCl_4. The metal carbonyls used were $Rh_6(CO)_{16}$, $Co_2(CO)_8$ and $Ru_3(CO)_{12}$. Each of the metal carbonyl complexes were anchored to a silica gel support via a phosphino-silane linkage. When the catalysts were employed for the hydrodechlorination of carbon tetrachloride a maximum of 3% conversion to chloroform was observed with only a small amount of hydrocarbons produced.

Finally, some work was performed on the homogeneous hydrogenation of carbon tetrachloride to prduce chloroform using

$[HCo(CN)_5]^{3-}$ as the hydrogenation catalyst. Preliminary work using $[HCo(CN)_5]^{3-}$ show that the carbon tetrachloride can be hydrodechlorinated to produce chloroform selectivly. More work needs to be performed using this catalyst system to make the reaction catalytic.

CHAPTER IV
CONCLUSION

The objective of the research which is reported in the preceding chapters was to prepare a new solid acid with stable tetrahedral aluminum sites. Using aluminum chloride as the precursor this objective was achieved, a new solid acid was prepared and employed as a catalyst for various acid catalyzed reactions. The characterization of the catalyst by IR spectroscopy demonstrated that there were both Bronsted and Lewis acid sites present on the catalyst surface. In addition to the detection of acid sites by IR spectroscopy the relative strength of the Lewis acid sites present on the catalyst were determined. From the results of the IR investigation it could be concluded that the catalysts prepared by the reaction of silica gel, a high silica zeolite, alumina or boron oxide with aluminum chloride in carbon tetrachloride contained the strongest acid Lewis acid sites. The strengths of the Lewis acid sites on these catalysts were comparable to the strengths of the Lewis acid sites on commercial cracking catalysts. If other solvents or inorganic oxides were used the catalyst obtained had a lower Lewis acidity. The characterization of the catalysts by ^{27}Al and ^{29}Si solid-state MAS NMR spectroscopy demonstrated that the catalysts prepared by the reaction of aluminum chloride and an inorganic oxide in CCl_4

contained tetrahedral chloroaluminum species that are stable under catalytic cracking reaction conditions.

The reactions involving the cracking of the hydrocarbons demonstrated the catalytic activity of the new solid acid catalysts. From the cracking reactions it could be concluded that the 50 wt% catalyst prepared on silica gel (340 m^2/gram surface area) and a high silica zeolite were the most active. Trends in the cracking activity of the catalysts paralleled the order of Lewis acid site strength as determined by the infrared studies. It was also determined that in order for long term activity to occur a chlorine source was needed. The formation of coke was detected during the cracking reactions and was the primary cause of catalyst deactivation. The addition of a noble metal to the solid acid catalyst increased the activity of the catalysts and increased the catalyst lifetime by reducing the formation of coke.

Other reactions studied involving hydrocarbons were polymerizations and the activation of methane. Results from the polymerization reactions indicated that the catalyst was a cationic polymerization initiator. From the results of the activation of methane by the solid acid catalyst it could be concluded that the solid acid is not strong enough to activate methane directly. Methane activation could occur from the reaction of methane with primary carbonium ions generated during the cracking of higher chain hydrocarbons. Since the formation of primary carbonium ions is unfavorable the activation of methane by this method is only minor.

In addition to cracking, the dehydrochlorination and hydrodechlorination of various polychlorinated hydrocarbons was studied. The heterogeneous hydrodechlorination of carbon tetrachloride by metal-doped solid acid catalysts indicated that the selcetive conversion of carbon tetrachloride to chloroform was feasible. High conversions could be obtained for the conversion of carbon tetrachloride to hydrocarbon products. The selective conversion to chloroform could only be obtained in the presence of a hydrocarbon. Promising results were obtained from the reactions involving the dehydrochlorination of 1,2-dichloroethane. The most selective catalyst was a $RuCl_3$-doped solid acid catalyst prepared on silica gel. A selectivity of 85% to vinyl chloride could be obtained at a reaction temperature of 200°C. The results from the dehydrochlorination reactions suggest that further work in this area may lead to a catalytic process for the conversion of 1,2-dichloroethane to vinyl chloride. Currently there is no commercial catalytic process for the conversion of 1,2-dichloroethane to vinyl chloride.

Work in the area of the homogeneous hydrodechlorination of carbon tetrachloride is only preliminary but suggests a promising alternative for the selective conversion of carbon tetrachloride to chloroform.

The research reported in this dissertation has opened new avenues of approach to old reactions. Several reactions which should be studied in more detail include the conversion of 1,2-dichloroethane to vinyl chloride, dehydration, alkylation and

acylation reactions. A strong supported Lewis acid, with discrete acid sites has the potential for the catalysis of many acid catalyzed reactions and warrents further investigation.

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